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THE UNIVERSITY OF ALBERTA
APPLICATIONS OF THE VARIATIONAL METHOD

by

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A THESIS

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A THESIS IN THREE PARTS

THE USE OF GAUSSIAN FUNCTIONS IN ATOMIC WAVE FUNCTIONS

OPEN-SHELL CONFIGURATIONS

THE VARIATIONAL APPROACH TO THE
DESCRIPTION OF NMR AND EPR PHENOMENA

ABSTRACT

Gaussian functions were used as a basis for the expansion of the orbitals and correlation function for the helium atom. The energy obtained with a wave function of orbitals only approached within 0.03% of the Hartree-Fock limit. Except for a slight rounding at the nuclei the density distribution was identical to that given by an expansion in STF. Introduction of the correlation function improved the energy markedly to within 0.4% of Pekeris' value. The correlation function found indicated a compaction of electron density and increased electron repulsion. A lower total energy was, however, achieved by an increase in the electron density at the nucleus. These results were achieved in all cases with a quite reasonable (at most six) number of terms in the expansions.

The formalism of a rather general SCF theory was extended to cover more cases. Virtual orbitals and ionization energies were investigated and a more general, where possible, formulation in terms of the general SCF theory given. The constancy of orbitals between neighbouring states, which is basic to certain uses of orbital energies, (i.e., ionization energy, excitation energy) was investigated for small atoms and, within the Pariser-Parr context, in polyatomic molecules. The orbitals were found to be similar in ground and ionized states and the constancy became better as the system became larger.

The implications of the use of the perturbation method in describing NMR and EPR phenomena were investigated. The treatment was found to lead to the acceptance of concepts, such as coupling constants and well defined spin states of electrons and nuclei, which obscure the fundamental nature of the phenomena. An alternative and fundamentally different variational approach was developed. With an illustrative system of two electrons and two protons the salient factors involved in the phenomena were investigated quite readily. A simple numerical example indicating the relation of electronegativity serves to illustrate the ease with which other relationships might be demonstrated.

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When change itself can give no more

'Tis easy to be true.

Sir Charles Sedley

Reasons for Constancy

PREFACE

While this research has been concerned with essentially distinct problems, each with its particular interest and pertinent results, the approach in all cases is pervaded with a desire to resolve problems for which there is no exact solution, with a description which can be brought closer to the exact description with the aid of the variational technique on some basis set.

In part of this work the representation of one-electron orbitals and of two-electron correlation functions with Gaussian basis sets is investigated. In another section variational calculations for open-shell configurations are investigated and in a final section in an attempt to provide a more satisfactory description of nuclear magnetic resonance and electron paramagnetic resonance phenomena the variational calculation of the spin functions of electrons and nuclei with spinors as basis functions is also considered.

TABLES OF CONTENTS

PART ONE THE USE OF GAUSSIAN FUNCTIONS IN ATOMIC WAVE FUNCTIONS

CHAPTER I DEVELOPMENT

I-1	Introduction	3
I-2	The Wave Function	4
I-3	The Variational Equation	6
I-4	The Pseudo-Eigenvalue Equation	7
I-5	Formulation of the Matrix Equation	9
I-6	Formulation of the Integrals	10
I-7	Self-Consistent Field Solutions	13
I-8	Variation of the Basis Set	14

CHAPTER II RESULTS AND DISCUSSION

II-1	The Orbital Representation	18
II-2	The Correlation Function Representation	20

PART TWO OPEN-SHELL CONFIGURATIONS

CHAPTER III THE GENERAL SCF THEORY

III-1	Introduction	37
III-2	The General Self-Consistent Field Equations	37
III-3	The LCAO Representation of the SCF Equations	39

CHAPTER IV FEATURES OF THE SCF FORMULATION

IV-1	Extension of the Formulation	42
------	------------------------------	----

IV-2	The Ionization Energy	42
IV-3	Virtual Orbital Energies	45

CHAPTER V ATOMIC APPLICATIONS

V-1	Introduction	49
V-2	The Wave Functions	49
V-3	The Integrals and the SCF Solution	50
V-4	Results and Discussions	52

CHAPTER VI MOLECULAR APPLICATIONS

VI-1	Introduction	57
VI-2	The Approximation of Orthogonal Basis Functions	57
VI-3	Implications	59
VI-4	Applications	59

PART THREE THE VARIATIONAL APPROACH TO THE DESCRIPTION OF NMR AND EPR PHENOMENA

CHAPTER VII IMPLICATIONS OF THE PERTURBATION APPROACH ON THE DESCRIPTION OF NMR AND EPR PHENOMENA

VII-1	Introduction	70
VII-2	The Hamiltonian	71
VII-3	Implications of the Perturbation Technique	74

CHAPTER VIII DEVELOPMENT OF THE VARIATIONAL DESCRIPTION

VIII-1	The Wave Function	80
VIII-2	The Variational Equations	82

VIII-3	Approximations	84
--------	----------------	----

CHAPTER IX ILLUSTRATION OF THE METHOD

IX-1	The Matrix Representations	87
IX-2	Analysis of the Matrix Equations	92
IX-3	Sample Calculation	94

BIBLIOGRAPHY		100
--------------	--	-----

APPENDIX I EVALUATION OF THE GAUSSIAN INTEGRALS

AI-1	The Density Kernel	104
AI-2	The Potential Energy Integral for Electron One	108
AI-3	The Kinetic Energy Integral	109
AI-4	Electronic Repulsion Integral	110
AI-5	Overlap Integral	113

APPENDIX II SOLUTION OF THE MATRIX EQUATIONS

AII-1	Solution of the Matrix Equations	118
AII-2	Schmidt Orthonormalization (SOMS)	119
AII-3	Jacobi Diagonalization of H'	120

APPENDIX III VARIATIONS OF THE BASIS SET

AIII-1	Mavle	123
--------	-------	-----

APPENDIX IV INTEGRALS FOR THE BASIS FUNCTIONS

α AND β

AIV-1	The S Matrices	125
AIV-2	The H Matrices	125

LIST OF TABLES

I	Parameters for the expansion for the non-correlated case	24
II	Radial distribution of electron density for the non-correlated case	25
III	Point distribution of electron density for the non-correlated case	26
IV	Parameters for the expansion for the correlated function	27
V	Probability distribution of $ \Psi(r_1, r_2=0.6) ^2$	28
VI	Point density distribution for the correlated function	29
VII	Constancy of the derived ionization energy	54
VIII	Coefficients for the occupied orbitals	55
IX	Coefficients for the orbitals in the arbitrary S matrix calculations	62
X	Arbitrary S matrix calculations	63
XI	Two-electron repulsion integrals	64
XII	Core integrals	65
XIII	Coefficients for the orbitals for the Pariser-Parr calculations	66
XIV	Ionization energies (au.) for the Pariser-Parr approximation	67
XV	Data for illustrating the relation between ΔT_{AB} and hyperfine splitting	96
XVI	Typical spin function parameters	97

LIST OF FIGURES

1.	Flow diagram of master program	16
2.	Radial distribution of electron density for the orbital of non-correlated functions	30
3.	Point distribution of electron density for the orbital of non-correlated functions	31
4.	Dependence of χ upon the interelectron distance r_{12}	32
5.	Comparison of the probability distribution $ \Psi(r_1, 0.6) ^2$, for the correlated and non- correlated function	33
6.	Comparison of point density distribution for correlated and non-correlated function	34
7.	Energy level diagram	98
8.	The relation between the hyperfine splitting and the difference in the electron density on two centers	99

PART ONE

THE USE OF GAUSSIAN FUNCTIONS IN ATOMIC WAVE FUNCTIONS

CHAPTER I

DEVELOPMENT

I-1 Introduction

Within the orbital approximation the application of the principle that any well behaved function can be represented in terms of a complete set of functions¹ and the use of the variational theorem² lead to wave functions which would more closely represent the exact description of a system. However, only with the advent of electronic computers has expansion of the basis set sufficient to yield accurate results become feasible.

Further improvement upon such an orbital description of a many-body system can be achieved by introducing interparticle coordinates into the argument of the wave function through a "correlation function". Here again an adequate representation of the correlation function can be obtained with an appropriate basis set.

Clearly it is possible to obtain rather accurate descriptions of systems given a sufficiently large basis set and time to perform the variational calculation; perhaps the best support for this approach is that Pekeris'³ calculated value for the energy of helium is now quoted instead of the experimental. However, except for the simplest systems, mathematical manipulations leading to the necessary integrals and the evaluation of these integrals may rapidly become intractible,* even with the aid of a

* Compare for example the formulation of the integrals of Roothaan and Weiss⁴ (for e^{-mr} basis functions) for helium to those of this work. The disparity is accented in more complex systems.

computer, unless care is exercised in the choice of the form of the basis functions.

The use of Gaussian functions as a basis for the variational calculation of orbitals comprising wave functions of atomic and molecular systems has been discussed by several authors^{5,6}. More recently the advantage of representing two-electron functions by expansions in Gaussian functions has been noted⁷. In both instances the mathematical manipulations, although complex, lead to analytic integrals (up to the error integral) and consequently facilitate the computational steps, thus admitting the possibility of the solution of the large problems of interest to the chemist.

Recognizing this advantage of the form of Gaussian basis functions, an investigation has been undertaken to determine whether a reasonable number of Gaussian functions can yield wave functions with an energy value comparable to that obtained from other sources, and whether a correlation function, which is an expansion in a set of Gaussian functions having the interelectron distance as the argument, can yield accurate energies.

The helium atom was used as the test case. The number of basis functions used was to some extent limited by the capabilities of the computer available.

I-2 The Wave Functions

The total wave function for the non-correlated case is

given as

$$\Psi = A\psi = A (\phi(1) \bar{\phi}(2))$$

where A is an antisymmetrizer and $\phi(1)$ and $\bar{\phi}(2)$ are spin-orbitals associated with spin α and β respectively. With ϕ written as $\varphi(1)\alpha(1)$ the orbital $\varphi(1)$ is represented by an expansion in Gaussians as

$$\varphi(1) = \sum_{i=1}^p c_i G_i(1), \quad G_i(1) = \exp(-m_i r_1^2);$$

p is the number of basis functions, and r_1 is distance of electron 1 from the nucleus.

For the correlated case the total wave function is given as

$$\Psi = A\psi = A (\phi(1) \bar{\phi}(2) \chi(12))$$

where the correlation function $\chi(12)$ is expanded as

$$\chi(12) = \sum_{s=1}^q d_s G_s(12), \quad G_s(12) = \exp(-m_s r_{12}^2);$$

q is the number of basis functions and r_{12} is the distance between electrons 1 and 2.

Since there are only two electrons the result of the antisymmetrizer is the same in both cases and can be written as the Slater determinant;

$$A\psi = \begin{vmatrix} \phi(1) & \bar{\phi}(1) \\ \phi(2) & \bar{\phi}(2) \end{vmatrix}, \quad A\psi = \begin{vmatrix} \phi(1) & \bar{\phi}(2) \\ \phi(2) & \bar{\phi}(1) \end{vmatrix} \chi(12)$$

Frequent reference will be made to the work of Roothaan and Weiss.⁴ Their total wave functions are formulated as above except that the expansions are:

$$\varphi(r) = \sum_{i=0}^m a_i \mu_i(r), \quad \mu_i(r) = (\xi r)^i e^{-\xi r}$$

$$\chi(r_{12}) = \sum_{\mu=0}^n c_{\mu} v_{\mu}(r_{12}) \quad , \quad v_{\mu}(r_{12}) = (\xi r_{12})^{\mu} \quad .$$

There can, of course, be no orthonormality constraint on the φ and χ .

I-3 The Variational Equation

The energy can be written in bra-ket notation as

$$E = \langle \Psi / H / \Psi \rangle / \langle \Psi / \Psi \rangle$$

where $H = -\sum_{i=1}^2 (\nabla_i^2 / 2 + \frac{2}{r_i}) + \frac{1}{r_{12}}$ with ∇_i^2 denoting

the Laplacian for the kinetic energy. An arbitrary variation in the energy is given by

$$\delta E = [\delta \langle \Psi / H / \Psi \rangle - E \delta \langle \Psi / \Psi \rangle] / \langle \Psi / \Psi \rangle$$

For the condition of minimum energy $\delta E = 0$, and since $\langle \Psi / \Psi \rangle$ must be finite one obtains

$$\delta \langle \Psi / H / \Psi \rangle - E \delta \langle \Psi / \Psi \rangle = 0$$

giving two equations which are Hermitian conjugates

$$\langle \Psi / H / \delta \Psi \rangle - E \langle \Psi / \delta \Psi \rangle = 0$$

$$\langle \delta \Psi / H / \Psi \rangle - E \langle \delta \Psi / \Psi \rangle = 0$$

The scalar products $\langle \Psi / H / \delta \Psi \rangle$ and $\langle \Psi / \delta \Psi \rangle$ may be simplified. $I = \langle \Psi / H / \delta \Psi \rangle = \langle A \psi / H / \delta A \psi \rangle$ and since the variations are independent of orbital occupancy one has $I = \langle A \psi / H / A \delta \psi \rangle = \langle A \psi / H A / \delta \psi \rangle$. For ψ real and $H A$ real and Hermitian $I = \langle \delta \psi / H A / A \psi \rangle = \langle \delta \psi / H / A^2 \psi \rangle$. But $A^2 \psi = K A \psi$ where K is a constant⁸ so that $I = K \langle \delta \psi / H / A \psi \rangle$. Similarly $\langle \Psi / \delta \Psi \rangle = K \langle \delta \psi / A \psi \rangle$.

Then $\langle \psi / H / \delta \psi \rangle - E \langle \psi / \delta \psi \rangle = K[\langle \delta \psi / H / A \psi \rangle - E \langle \delta \psi / H / A \psi \rangle] = 0$

Since $K \neq 0$ this gives as the variational equation

$$\langle \delta \psi / H / A \psi \rangle - E \langle \delta \psi / A \psi \rangle = 0$$

I-4 The Pseudo-Eigenvalue Equations

The variation $\langle \delta \psi /$ may be written for the non-correlated case as $\langle \delta \psi / = \langle \frac{\partial \psi}{\partial \varphi} / \delta \varphi$ and for the correlated case as $\langle \delta \psi / = \langle \frac{\partial \psi}{\partial \varphi} / \delta \varphi + \langle \frac{\partial \psi}{\partial \chi} / \delta \chi$. Here $\langle \frac{\partial \psi}{\partial \varphi} / \delta \varphi$ represents the variation in the bra $\langle \psi /$ when φ is given the arbitrary variation $\delta \varphi$.

For the correlated case the variations $\delta \varphi$ and $\delta \chi$ are independent and the variational equation can be written as two coupled equations.

$$\delta \chi [\langle \frac{\partial \psi}{\partial \chi} / H / A \psi \rangle - E \langle \frac{\partial \psi}{\partial \chi} / A \psi \rangle] = 0 \quad \text{I-1}$$

$$\delta \varphi [\langle \frac{\partial \psi}{\partial \varphi} / H / A \psi \rangle - E \langle \frac{\partial \psi}{\partial \varphi} / A \psi \rangle] = 0 \quad \text{I-2}$$

By virtue of the linear expansion form chosen for φ and χ each of the above equations may be broken up into a set of equations which in turn can be represented by a single matrix equation.

In the first equation $\delta \chi \langle \frac{\partial \psi}{\partial \chi} /$ can be written as $\delta \chi \langle \frac{\partial \psi}{\partial \chi} / = \sum_{s=1}^q (\delta d_s) \langle \frac{\partial \psi}{\partial d_s} /$ and since the δd_s are independent, the equation becomes

$$\delta d_s [\langle \frac{\partial \psi}{\partial d_s} / H / A \psi \rangle - E \langle \frac{\partial \psi}{\partial d_s} / A \psi \rangle] = 0, \quad s = 1, q.$$

Further, since each δd_s is arbitrary then in each of the above equations the quantity within the square bracket must equal zero.

The scalar products can be expanded as

$$\left\langle \frac{\partial \Sigma_d \exp[-n_s r_{12}^2]}{\partial d_s} / H / \Sigma_s^q, d_s, \exp[-n_s, r_{12}^2] A \emptyset \bar{\emptyset} \right\rangle$$

which on differentiation becomes the sum of scalar products

$$\Sigma_s^q, \langle \exp[-n_s r_{12}^2] \emptyset \bar{\emptyset} / H / d_s, \exp[-n_s, r_{12}^2] A \emptyset \bar{\emptyset} \rangle \equiv \Sigma_s^q, H_{ss}^d, .$$

The two terms in each of the above equations become a sum of terms and one obtains the set of equations

$$\Sigma_s^q, (H_{ss}^d, d_s, - E S_{ss}^d, d_s,) = 0, \quad s = 1, q,$$

or the equivalent form, the matrix equation

$$\underline{H}^d \vec{d} = E \underline{S}^d \vec{d} \quad \text{I-3}$$

where $\vec{d}$ is a vector. $\underline{H}^d$ and $\underline{S}^d$ are matrices with elements:

$$H_{ss}^d, = \langle \exp[-n_s r_{12}^2] \varphi(1) \varphi(2) / H / \exp[-n_s, r_{12}^2] \varphi(1) \varphi(2) \rangle$$

$S_{ss}^d, = \langle \exp[-n_s r_{12}^2] \varphi(1) \varphi(2) / \exp[-n_s, r_{12}^2] \varphi(1) \varphi(2) \rangle$ where the spin has been integrated out for a spin-independent hamiltonian

When the variation $\langle \frac{\partial \psi}{\partial \varphi} / \delta \psi$ is written as

$$\left\langle \frac{\partial \psi}{\partial \varphi} / \delta \psi \right\rangle = \left\langle \frac{\partial (\varphi_1 \varphi_2 \chi)}{\partial \varphi_1} / \delta \varphi_1 \right\rangle + \left\langle \frac{\partial (\varphi_1 \varphi_2 \chi)}{\partial \varphi_2} / \delta \varphi_2 \right\rangle = 2 \left\langle \frac{\partial \varphi_1 \varphi_2 \chi}{\partial \varphi_1} / \delta \varphi_1 \right\rangle$$

the matrix formulation of equation (I-2) can be developed in a manner analogous to the above to give

$$\underline{H}^c \vec{c} = E \underline{S}^c \vec{c} \quad \text{I-4}$$

where $\vec{c}$ is a vector. $\underline{H}^c$ and $\underline{S}^c$ are matrices with elements, after integration of spin, as

$$H_{ii}^c = \langle \exp[-m_i r_1^2] \mathcal{P}(2) \chi(12) / H / \exp[-m_i r_1^2] \mathcal{P}(2) \chi(12) \rangle$$

$$S_{ii}^c = \langle \exp[-m_i r_1^2] \mathcal{P}(2) \chi(12) / \exp[-m_i r_1^2] \mathcal{P}(2) \chi(12) \rangle$$

Equation(I-4) is the matrix eigen-function formulation of the variational problem for the non-correlated case.

The two matrix equations

$$\underline{H}^d \underline{\vec{d}} = E \underline{S}^d \underline{\vec{d}} \quad \text{and} \quad \underline{H}^c \underline{\vec{c}} = E \underline{S}^c \underline{\vec{c}}$$

with the common eigenvalue E , are taken as the statements of the variational problem for the correlated case.

I-5 Formulation of the Matrix Elements

On substitution for $\mathcal{P}$ and χ the scalar product matrix elements of the foregoing may be expanded and written in integral form. For the correlated case:

$$H_{ss'}^d = \sum_i \sum_{i'} \sum_j \sum_{j'} c_i c_{i'} c_j c_{j'} H_{ii'jj'ss'}$$

$$H_{ii'}^c = \sum_j \sum_{j'} \sum_s \sum_{s'} c_j c_{j'} d_s d_{s'} H_{ii'jj'ss'}$$

$$S_{ss'}^d = \sum_i \sum_{i'} \sum_j \sum_{j'} c_i c_{i'} c_j c_{j'} S_{ii'jj'ss'}$$

$$S_{ii'}^c = \sum_j \sum_{j'} \sum_s \sum_{s'} c_j c_{j'} d_s d_{s'} S_{ii'jj'ss'}$$

where

$$H_{ii'jj'ss'} = \int \exp[-m_i r_1^2 - m_j r_2^2 - n_s r_{12}^2] \\ \exp[-m_{i'} r_1^2 - m_{j'} r_2^2 - n_{s'} r_{12}^2] d\hat{c}$$

$$S_{ii'jj'ss'} = \int \exp[-m_i r_1^2 - m_j r_2^2 - n_s r_{12}^2] \\ \exp[-m_{i'} r_1^2 - m_{j'} r_2^2 - n_{s'} r_{12}^2] d\hat{c}$$

and $d\mathcal{C}$ represents the volume element for all space for the two electrons.

For the non-correlated case there is only the one matrix equation, $\underline{H}^{\mathcal{C}}\vec{c} = E\underline{S}^{\mathcal{C}}\vec{c}$, and the elements reduce to

$$H_{ii'}^{\mathcal{C}} = \sum_j \sum_{j'} c_j c_{j'} H_{ii'jj'}, \quad S_{ii'}^{\mathcal{C}} = \sum_j \sum_{j'} c_j c_{j'} S_{ii'jj'}$$

where

$$H_{ii'jj'} = \int \exp[-m_i r_1^2 - m_j r_2^2] H \exp[-m_{i'} r_1^2 - m_{j'} r_2^2] d\mathcal{C}$$

$$S_{ii'jj'} = \int \exp[-m_i r_1^2 - m_j r_2^2] \exp[-m_{i'} r_1^2 - m_{j'} r_2^2] d\mathcal{C}.$$

I-6 Formulation of the Integrals

The matrix elements of the foregoing lead to integrals of the form

$$I = \int \exp[-\sum_i a_i r_i^2 - \sum_{ij} b_{ij} r_{ij}^2] \\ \underline{M} \exp[-\sum_k a_k r_k^2 - \sum_{kl} b_{kl} r_{kl}^2] d\mathcal{C}$$

where $\underline{M}$ is some operator.

Boys^{5,7} has developed, in a series of papers, a general method of evaluating integrals of this form. Although much of this method depends upon the execution of the proper mathematical manipulations at the proper time, there is in addition the introduction of the density kernel, which allows both the very elegant formulation of the integrals, and subsequently the ease of their solution.

The density kernel allows an integral $\langle \Phi_1 / Q / \Phi_2 \rangle$, where Φ is a function of many electron co-ordinates and Q is a sum of one electron operators, to be expressed as a sum of integrals $\langle \phi_i / Q_i / \phi_j \rangle$ where the ϕ_i are functions only of

the electron involved in Q_i . Thus the density kernel operator for electron i involves integration over the coordinates of all other electrons and retains the identity of the coordinate of electron i as belonging either to the bra or to the ket. This last requirement is necessary since certain of the operators Q_i will be differential operators and act only on the coordinates of $\underline{r}_i$ in either the bra or ket but not both.

Letting $P(x'/x'')$ denote the operator replacing x'' by x' , then the density kernel operator $R(\vec{r}', \vec{r}'', i)$ for electron i is defined by

$$\begin{aligned} \langle \emptyset_1 / R(\vec{r}', \vec{r}'', i) / \emptyset_2 \rangle &= \left(\pi^N \prod_{j \neq i} \int d\vec{r}_j \right) P(\vec{r}' / \vec{r}_i) \emptyset_1 P(\vec{r}'' / \vec{r}_i) \emptyset_2 \\ &= c_i f_i(\vec{r}' \vec{r}'') \end{aligned}$$

so that this operation denotes coordinates of electron i coming from the bra as $\underline{r}'$ and those from the ket as $\underline{r}''$ and integrates over the others to give the factor c_i . Then the integral

$$\langle \emptyset_1 / \Sigma_i Q_i / \emptyset_2 \rangle = \int d\vec{r} P(\vec{r} / \vec{r}') P(\vec{r} / \vec{r}'') Q(\vec{r}'') \Sigma_i \langle \emptyset_1 / R(\vec{r}', \vec{r}'', i) / \emptyset_2 \rangle .$$

It will be noticed that the operator Q_i has been moved to the left of the coordinates of the bra and ket but since the density kernel operator has denoted the coordinates of electron i coming from the bra as $\underline{r}'$ and those coming from the ket as $\underline{r}''$ then the operator Q_i need only be expressed as $Q(\underline{r}'')$ in order that it operate correctly. Once the operation by Q has been performed there is no longer any need for distinction between $\underline{r}'$ and $\underline{r}''$ and so the operators $P(\vec{r} / \vec{r}')$ and $P(\vec{r} / \vec{r}'')$ operate on $\underline{r}'$ and $\underline{r}''$ leaving the integral

$\int d\vec{r} F(\vec{r})$ to be evaluated. $F(\vec{r})$ is the result of $Q(\vec{r}'')$ operating on $\sum_i c_i f_i(\vec{r}, \vec{r}'')$ followed by operation by the P 's, i.e., $F(\vec{r}) = P(\vec{r}/\vec{r}') P(\vec{r}/\vec{r}'') Q(\vec{r}'') \sum_i c_i f_i(\vec{r}, \vec{r}'')$.

The utility of this form can be appreciated when it is noted that the integrals for several operators $Q_i = -\nabla_i^2, \frac{1}{r_i}$ etc., can be evaluated using the same density kernel.

Boys' general approach is particularized to the helium system in Appendix I. When the hamiltonian is separated into kinetic energy, nuclear attraction and repulsion of the two electrons the integrals, as developed in Appendix I, have the forms listed below. It is worthwhile emphasizing that the integrals listed are all analytic.

$$H_{ii'jj'ss'} = \frac{H(KE1)}{ii'jj'ss'} + \frac{H(KE2)}{ii'jj'ss'} + \frac{H(NA1)}{ii'jj'ss'} + \frac{H(NA2)}{ii'jj'ss'} + \frac{H(Rep)}{ii'jj'ss'}$$

$$\frac{H(KE1)}{ii'jj'ss'} = G_1 \frac{3(a_1 b_1 + b_1 c_1 + c_1 a_1)}{(a_1 + b_1)^{5/2}} \pi^{3/2}$$

$$\frac{H(KE2)}{ii'jj'ss'} = G_2 \frac{3(a_2 b_2 + b_2 c_2 + c_2 a_2)}{(a_2 + b_2)^{5/2}} \pi^{3/2}$$

$$\frac{H(NA1)}{ii'jj'ss'} = \frac{2\pi G_1}{a_1 + b_1}$$

$$\frac{H(NA2)}{ii'jj'ss'} = \frac{2\pi G_2}{a_2 + b_2}$$

$$\frac{H(Rep)}{ii'jj'ss'} = \frac{2\pi^{5/2} (U + V)^{-1/2}}{UV + UW + VW}$$

$$S_{ii'jj'ss'} = (UV + W(U + V))^{-3/2} \pi^3$$

where:

$$G_1 = \pi^{3/2} (m_j + m_{j'} + n_s + n_{s'})^{-3/2}$$

$$G_2 = \pi^{3/2} (m_i + m_{i'} + n_s + n_{s'})^{-3/2}$$

$$a_1 = m_i + n_s - \frac{n_s (n_s + n_{s'})}{m_j + m_{j'} + n_s + n_{s'}}$$

$$a_2 = m_j + n_s - \frac{n_s (n_s + n_{s'})}{m_i + m_{i'} + n_s + n_{s'}}$$

$$b_1 = m_{i'} + n_{s'} - \frac{n_{s'} (n_s + n_{s'})}{m_j + m_{j'} + n_s + n_{s'}}$$

$$b_2 = m_{j'} + n_{s'} - \frac{n_{s'} (n_s + n_{s'})}{m_i + m_{i'} + n_s + n_{s'}}$$

$$c_1 = \frac{n_s n_{s'}}{m_j + m_{j'} + n_s + n_{s'}}$$

$$c_2 = \frac{n_s n_{s'}}{m_i + m_{i'} + n_s + n_{s'}}$$

$$U = m_i + m_{i'}, \quad V = m_j + m_{j'}, \quad W = n_s + n_{s'}$$

I-7 Self-Consistent Field Solutions

A basis program to calculate the matrix elements was written for the IBM 1620 and 7090.

Solutions of the matrix equations for the eigenvectors and eigenvalues were carried out by performing a Schmidt Orthonormalization followed by a Jacobi diagonalization and a search for the lowest eigenvalue and eigenvector. These steps are examined in detail in Appendix II.

Using the basis program in conjunction with programs for the procedures mentioned above, a master program was

constructed which solved the matrix equations given by a set of basis functions and trial vectors for a new set of vectors. These last vectors then became the trial vectors and the calculation of the matrix elements and solution of the matrix equations was repeated until the output and input vectors were the same to five figures. The vectors and energy found at this point were taken to be the self-consistent field (SCF) values for a given basis set. Figure 1 presents a flow diagram of the master program with associated programs.

I-8 Variation of the Basis Set

Variation of the exponential parameters $\underline{m}$ and $\underline{n}$ of the Gaussian basis sets was attempted by two associated programs. The first of these, referred to as "Mavle", varied one parameter at a time until a temporary best value of that parameter was found and then continued on to the next parameter, and so on returning finally to the first parameter and repeating the cycle until the best value of all parameters had been found. The second, the method of quadratic minimization, is a method of solving for the best exponential parameters when the energy surface in the space of the exponential parameters had been mapped in the region of the minimum. The first procedure is examined in detail in Appendix III and the second has been discussed in some detail by Ransil.⁹ Of the two methods the former, somewhat less elegant procedure, was found to be the most satisfactory. Additional provision was made for varying the basis

set by changing the number of terms in either or both of the orbital and correlation expansions. The storage capacity of the machine limited this flexibility.

I-9 Electron Density

Three forms of the electron density were used in an effort to provide insight into the detailed character of the wave function.

Defining the Radial Electron Density as

$$RD(r_2) = \left[\int \Psi^2 d\tau_1 \sin \theta_2 d\theta_2 d\phi_2 \right] r_2^2$$

gives $RD(r_2) = \bar{G}_2 4\pi r_2^2$ where $\bar{G}_2$ is the density kernel for electron two.

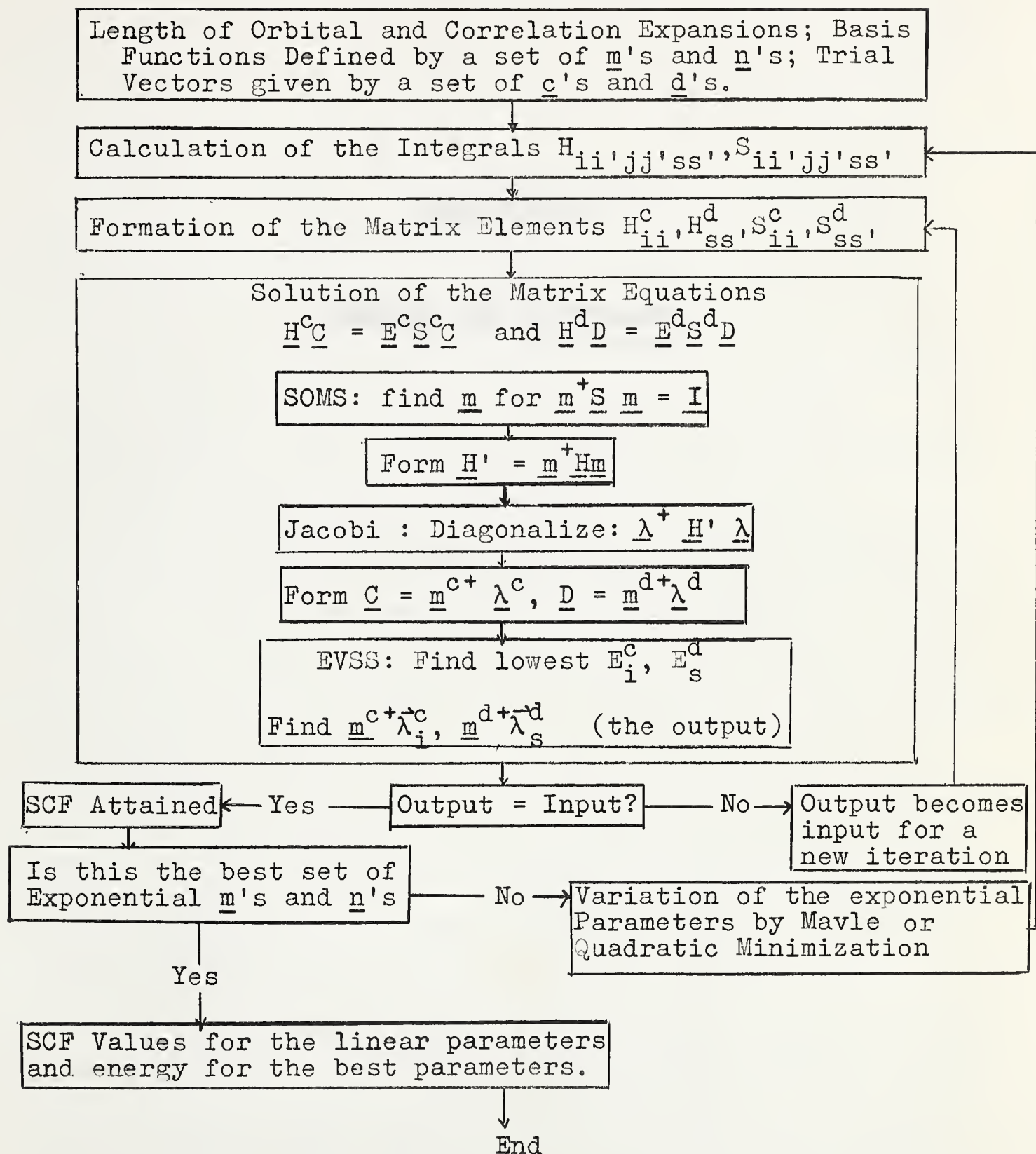
The Point Electron Density is defined as

$$PD(r_2) = \int \Psi^2 d\tau_1 = \bar{G}_2$$

The appropriate form of $\bar{G}_2$, as given in section AI-1, was inserted into these formulae and a program written to calculate the densities for various values of $\underline{r}$.

The program could be modified to provide $|\Psi(r_1, r_2)|^2$ allowing the probability function to be investigated for particular values of both electron coordinates.

Figure 1

Flow Diagram of Master Program

CHAPTER II

RESULTS AND DISCUSSION

II-1 The Orbital Representation

Table I displays the best exponential parameters, SCF coefficients, and energies found for the non-correlated wave functions when the orbitals are given by one-to six-term expansions in Gaussians.

A comparison of the energies given in column nine indicates that further expansion of the basis set would improve the energy only slightly.

The best energy achieved here differs by only 0.03% from the Hartree-Fock energy of -2.862 au.^{*}, which is in addition, the best energy of Roothaan and Weiss using a five-term expansion in restricted Slater functions.

In view of this one may conclude that a reasonable number of terms (five or six) in a Gaussian expansion gives energies for the helium atom which are close to those using Slater functions and which compare favourably to the Hartree-Fock energy.

The radial density distributions and the point density distributions are displayed in Tables II and III and figures 2 and 3 for several of these expansions and for the single- and four-term Slater expansion of Roothaan and Weiss.¹⁰

It is apparent that the effect of increasing the number of terms in the Gaussian expansion from three to six is, as viewed from the point density plot, to raise the electron

^{*}Throughout this thesis au. refers to Hartree Atomic Units (i.e. 1 au. = 27.204 ev).

density in the region of the nucleus (with a slight increase in the slope), and, from the radial distribution plot, to move the maximum somewhat closer to the nucleus - clearly an attempt to correct for the zero slope of the Gaussian form at the nucleus. On the other hand the increase in the number of terms in the Slater expansion is effecting an increase in the density about the nucleus (with slight decreases in the slope) and flattening the radial distribution curve - in this case an attempt to correct for rather peaked character of the Slater function. However, the distributions as given by the best Slater and best Gaussian expansions are essentially the same, an indication that although the Gaussian expansion is approaching the representation of the orbital from a different direction than the Slater expansion, the result is the same.

One might have expected the inadequacy of the Gaussian form in the region of the nucleus to preclude a good 1S orbital representation or indeed even an approach to the Slater representation. However, in view of these results, one may suggest that a Gaussian expansion can represent adequately the 1S type of orbital with a reasonable number of terms.

In regions further from the nucleus the Gaussian form would be more plausible¹¹ and representations of 2S, 2P-type functions with basis functions of the form $r^2 \exp[-mr^2]$ and $z \exp[-nr^2]$, etc., should be practicable - certainly as feasible as with Slaters - so that Gaussians give promise

of an adequate representation of the orbitals for many-electron problems.

II-2 The Correlation Function Representation

Correlation functions given by two-, four-, and six-term expansions were associated with one-electron protions generated by one-, three-, and six-term expansions to give the correlated wave function. Table IV displays the best exponential parameters, SCF coefficients and the energies.

The best energy obtained is 0.4% above Pekeris,³ value and 0.3% above the best value of Roothaan and Weiss with their correlation function for a closed shell function. A comparison of the energies for $p=2$; $q=2,4$, and 6 in the table indicates that extension of the basis set for the correlation function beyond the first two terms improves the energy only very slightly.

It is clear then, that an improvement in the energy (some 71% of the difference between Hartree-Fock and experimental), comparable to that using other functions can be produced by a correlation function given by a quite small expansion in Gaussians.

In all cases the introduction of the two-electron variable results in an improvement in the energy. The source of this improvement may now be investigated.

The χ function given in the tables is depicted schematically in figure 4. The classical form of the function of Hartree and Ingman¹² which has a minimum for

$r_{12}=0$ and a finite limit for $r_{12} \rightarrow \infty$, and the χ function determined by Roothaan and Weiss are given for comparison in the same figure.

The Gaussian correlation function does not introduce a lowering of weight of the wave function on close approach of the two electrons which both the Roothaan and Weiss and the Hartree and Ingman functions would accomplish. It does, however, approach an asymptotic value as $r_{12} \rightarrow \infty$, as required classically, while the Roothaan and Weiss function goes to $+\infty$.

Although both the Roothaan and Weiss and the Gaussian correlation functions imply a quite non-classical behaviour, the inadequacy of the former would not necessarily be important for the over all description since the orbital parts would certainly cause the total function to go to zero as $r_{12} \rightarrow \infty$ suggesting a well behaved total wave function. Such a happy resolution of the problem is not possible in the Gaussian case.

The behaviour of the total wave function with Gaussian functions can be investigated by a comparison of the curves for the correlated and non-correlated functions, for the variation of $|\Psi(r_1, r_2=0.6)|^2$ as the coordinate r_1 is changed along a line through electron two and the nucleus. As figure 5 shows there is an increased probability for the first electron in the region of the second compared to the probability for the same radial distance on the opposite side of the nucleus. Indeed the most probable

position of the first electron is between the nucleus and the other electron, not as one might have expected, on the opposite side. Clearly the introduction of explicit dependence on the interelectron distance with Gaussians is inducing a compactness of the electrons - a behaviour which is imposed essentially by the χ function alone.

Such a compaction and accompanying increased repulsion can result in an overall lowering of the energy if the build-up can be made to occur closer to the nucleus. Comparison of the energies between Tables I and IV shows that the improvement in the energy with correlation is most marked the larger the expansion for the one-electron part. But, as the curves of figures 3 and 6 show, the larger the expansion the greater the density at the nucleus, hence a greater improvement on correlation. Further, comparison of the exponents of the one-electron parts of the correlated and non-correlated functions as given by Tables I and IV indicates a tendency for an increase in the electron density for the correlated case in the region of the nucleus - a behaviour, at least for the orbital, quite the opposite to that in Roothaan and Weiss' best function. It might be pointed out here that for the poorer functions of Roothaan and Weiss a similar behaviour (the orbital exponent increase) occurs with correlation - an indication that condensation, even with their function, can be a first step toward energy improvement.

It appears then that the correlation obtained here is not toward a decrease in the weighting of the function for

$r_{12} \rightarrow 0$. Rather it is an attempt to improve on the energy by a compensatory process - the compaction of the electrons, and resulting repulsion, being compensated for by a greater nuclear attraction.

That the improvement in the energy must be produced by such non-classical correlation may be due to the Gaussian form of either the one-electron functions or the correlation function itself. The investigation of a Gaussian correlation function with one-electron functions given by Slaters would certainly shed some light on this aspect.

Although the source of improvement in the energy is questionable one may suggest that improvement in the energy with a correlation function given by an expansion in Gaussians is feasible.

Table I

Parameters* for the expansion for the non-correlated case.

	Parameter type	1	2	3	4	5	6	Energy (au.)
1	c	0.268						
	m	0.767						-2.301
2	c	0.366	0.581					
	m	0.532	0.410					-2.747
3	c	0.228	0.490	0.406				
	m	0.383	2.00	13.6				-2.836
4	c	0.143	0.389	0.413	0.265			
	m	0.293	1.21	5.59	37.0			-2.855
5	c	0.090	0.302	0.386	0.304	0.177		
	m	0.235	0.820	3.06	13.4	88.6		-2.860
6	c	0.052	0.215	0.335	0.326	0.226	0.128	
	m	0.189	0.564	1.77	6.14	26.3	170.0	-2.861

* The energy to four figures is insensitive to changes of two to seven parts in the third figure of the exponential parameters m and to one part in the third figure in the linear coefficients c.

Table II

Radial distribution of electron density
for the non-correlated case.

Radius (a_0)	One Optimized Slater	Roothaan and Weiss	Gaussian Expansions 3	6
0	0	0	0	0
0.1	0.137	0.152	0.142	.152
0.2	-	0.413	0.418	0.414
0.3	0.628	0.639	0.635	0.637
0.4	-	0.786	0.764	0.783
0.5	0.889	0.856	0.844	0.857
0.6	0.914	0.865	0.877	0.866
0.7	0.888	0.832	0.860	0.831
0.8	-	0.772	0.800	0.772
0.9	-	0.699	0.712	0.700
1.0	0.658	0.621	0.619	0.625
1.1	-	0.543	0.533	0.547
1.2	-	0.469	0.457	0.473
1.4	0.326	0.341	0.340	0.345
1.6	-	0.240	0.252	0.244
1.8	0.094	0.166	0.181	0.163

Table III

Point distribution of electron density
for the non-correlated case.

Radius (a_0)	One Optimized Slater	Roothaan and Weiss	Gaussian Expansions 3	6
10^{-4}	-	1.741	1.261	1.628
0.05	-	1.463	1.226	1.477
0.1	1.008	1.210	1.126	1.210
0.2	-	0.834	0.836	0.834
0.3	0.558	0.562	0.561	0.562
0.4	-	0.391	0.380	0.389
0.5	0.282	0.273	0.268	0.273
0.6	0.202	0.101	0.194	0.191
0.7	0.144	0.135	0.139	0.135
0.8	-	0.096	0.099	0.096
0.9	-	0.069	0.070	0.069
1.0	0.052	0.050	0.049	0.050
1.1	-	0.036	0.036	0.036
1.2	-	0.026	0.026	0.026
1.4	0.013	0.014	0.014	0.014
1.6	-	0.007	0.007	0.007
1.8	0.002	0.001	0.001	0.001

Table IV

Parameters* for Gaussian expansion for the correlated function.

p	q	Parameter type	#	Parameter 2	position in the 3	4	5	6	Energy (au.)
1	c		0.334						
	m		0.818						
2	d		87.7	-84.7					-2.320
	n		0.	0.005					
3	c		0.082	0.174	0.144				
	m		0.367	2.0	13.9				
2	d		6.51	1.91					-2.855
	n		0.	0.35					
3	c		0.082	0.170	0.144				
	m		0.369	1.98	13.5				
4	d		6.32	0.882	0.725	0.695			-2.857
	n		0.	0.15	0.35	0.55			
3	c		0.080	0.166	0.139				
	m		0.371	2.00	13.6				
6	d		0.52	0.839	1.03	0.681	0.304	-0.753	-2.859
	n		0.	0.83	0.33	0.64	1.2	6.8	
6	c		0.106	0.199	0.297	0.317	0.244	0.144	
	m		0.239	0.692	1.79	5.56	22.2	147.	
2	d		0.746	0.278					-2.891
	n		0.	0.34					

*The sensitivity of the energy to the parameters is the same for the c and m as in Table I, for the d and s the energy is somewhat less sensitive.

#Although complete flexibility was allowed in the determination of the parameter n_1 the best value in all cases was effectively zero.

Table V

Probability distribution of $|\Psi(r_1, r_2 = 0.6)|^2$.

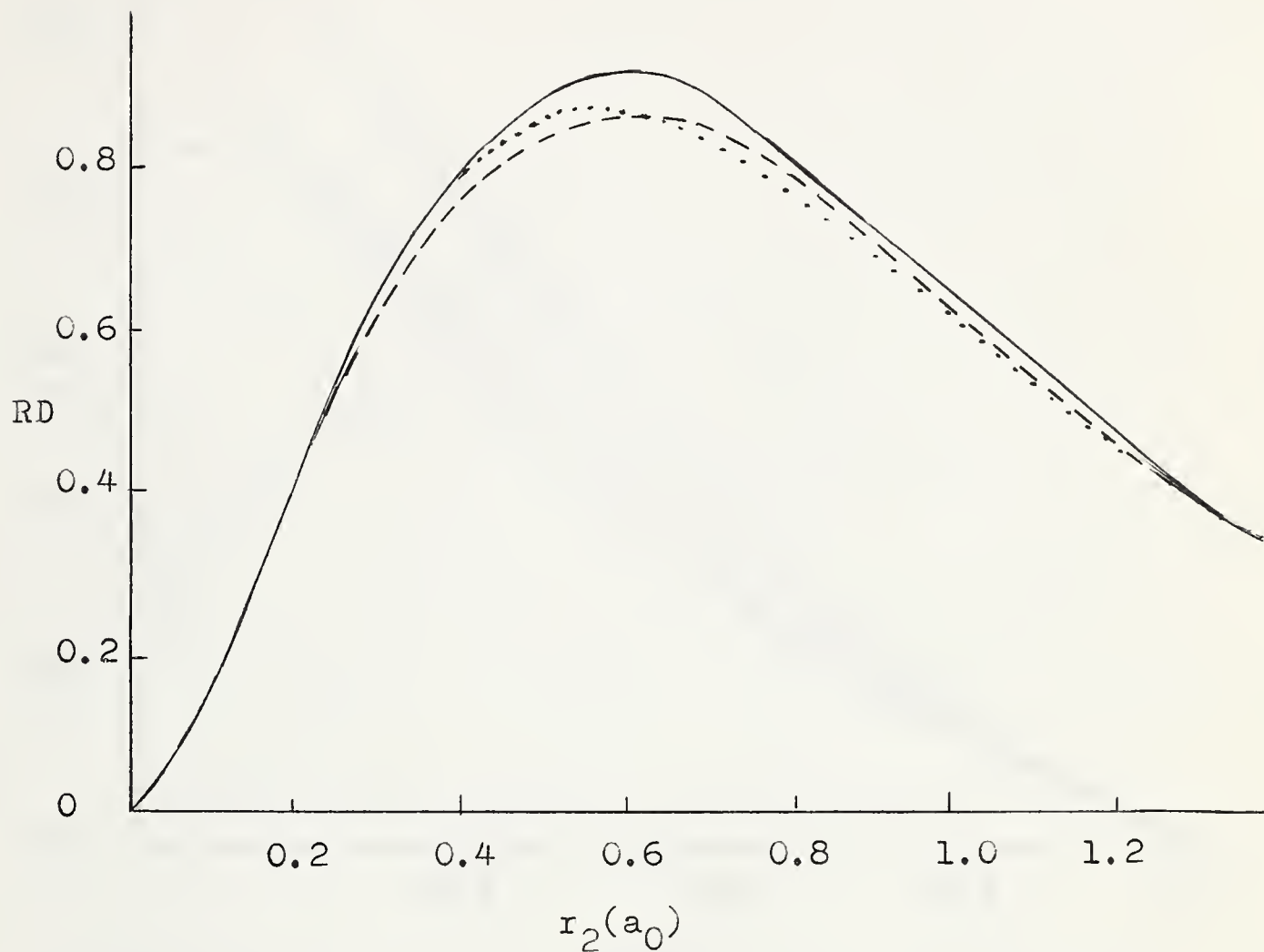
$r_1(a_0)$	Gaussian expansion	
	Correlated $p = 3, q = 2$	Non-correlated $p = 3$
-0.7	0.025	0.027
-0.5	0.051	0.052
-0.3	0.111	0.109
-0.1	0.234	0.219
0.0	0.267	0.245
0.1	0.261	0.219
0.3	0.123	0.109
0.5	0.060	0.052
0.7	0.032	0.027

Table VI

Point density distribution for the correlated function.

Radius (a_0)	Gaussian expansions	
	p q	6 2
0	1.700	1.317
0.1	1.258	1.198
0.2	0.859	0.801
0.3	0.584	0.560
0.4	0.402	0.390
0.5	0.280	0.274
0.6	0.195	0.197
0.7	0.139	0.141
0.8	0.097	0.099
1.0	0.049	0.049
1.2	0.025	0.025
1.4	0.013	0.013
1.6	0.007	0.007

Figure 2

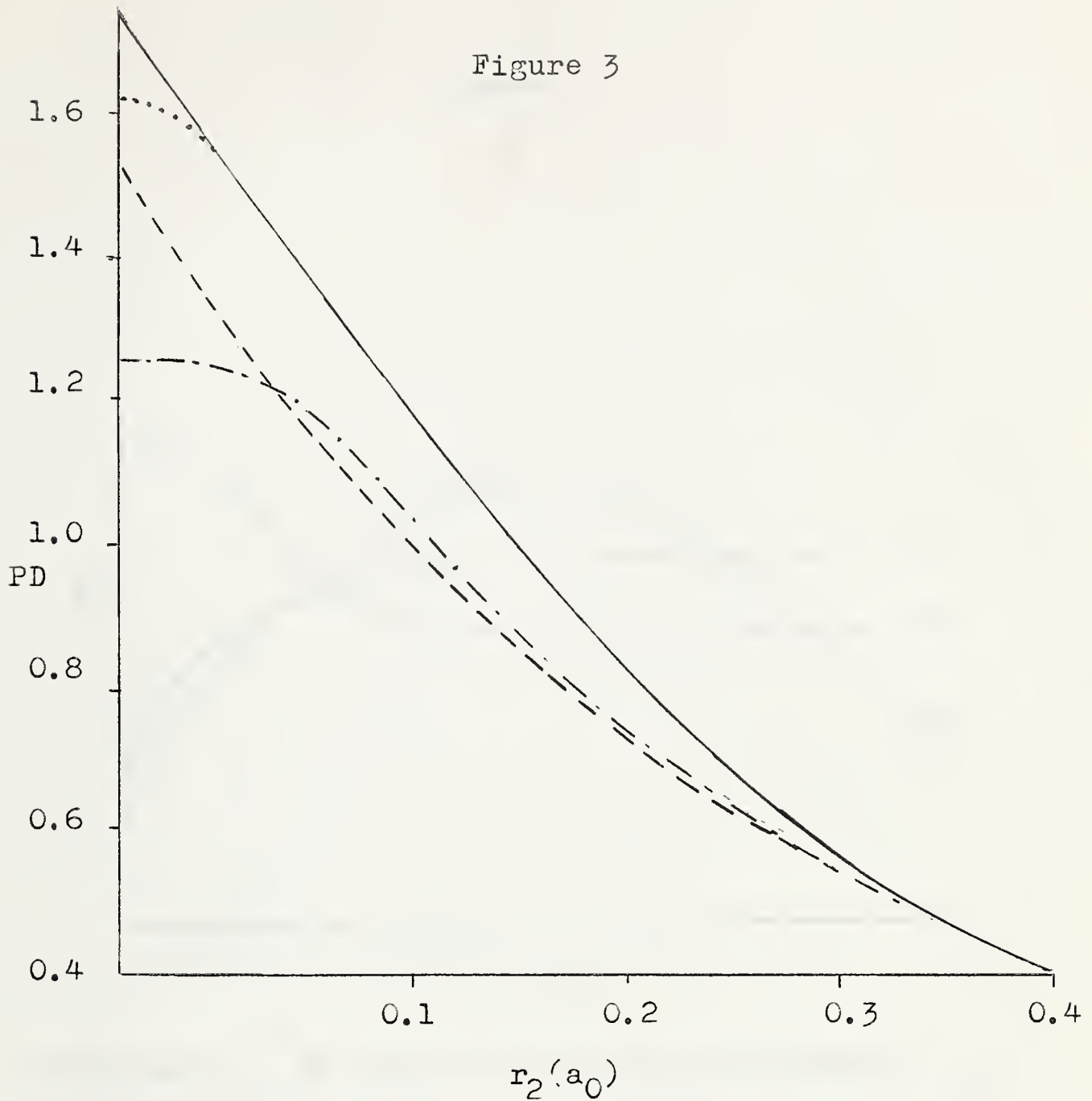


Radial distribution of electron density for
the orbital of non-correlated functions

Legend:

Roothaan and Weiss	}
Six-term Gaussian	
One optimized Slater	_____
Three-term Gaussian	-----

Figure 3



Point distribution of electron density
for the orbital of non-correlated functions

Legend:

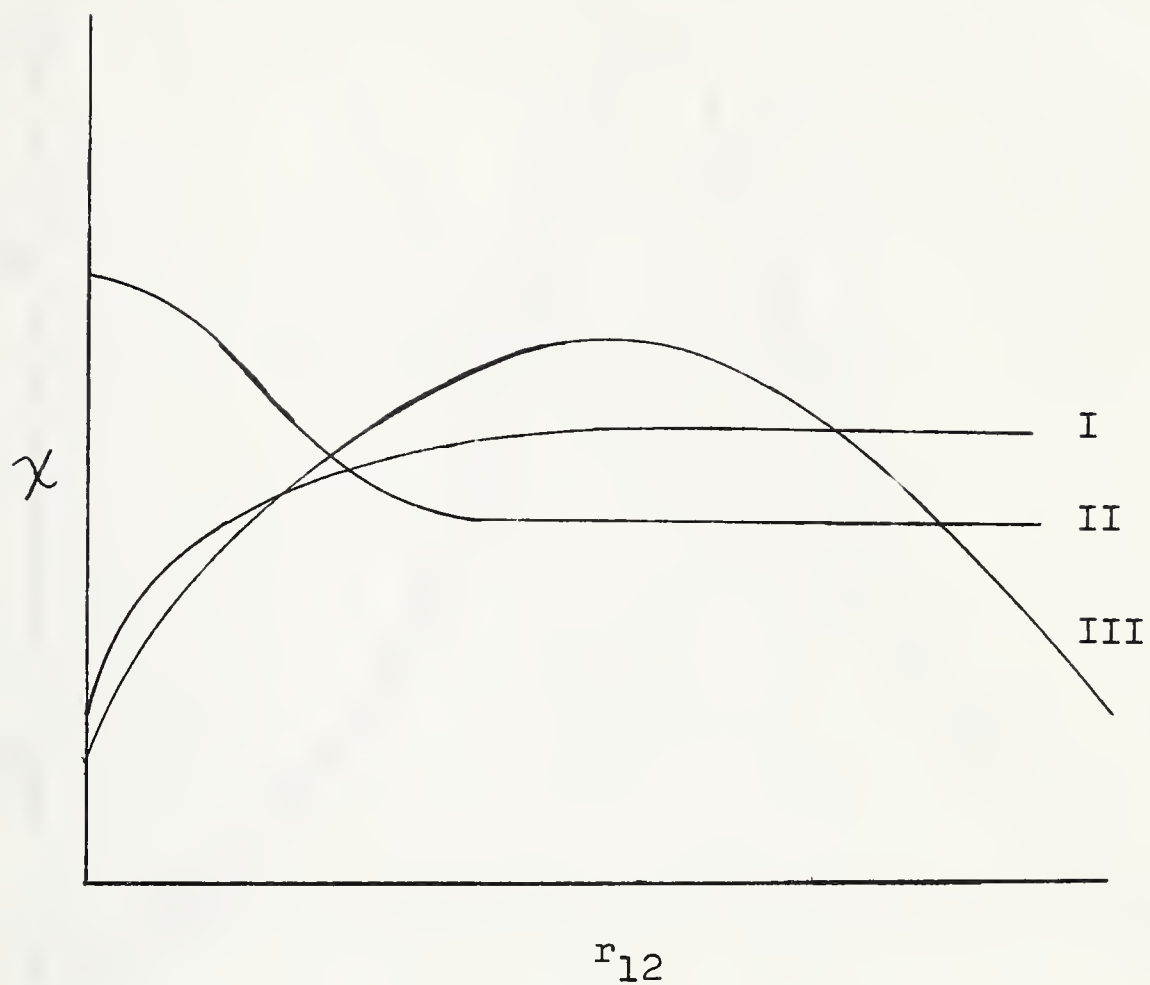
Roothaan and Weiss

Six-term Gaussian

One optimized Slater

Three-term Gaussian

Figure 4

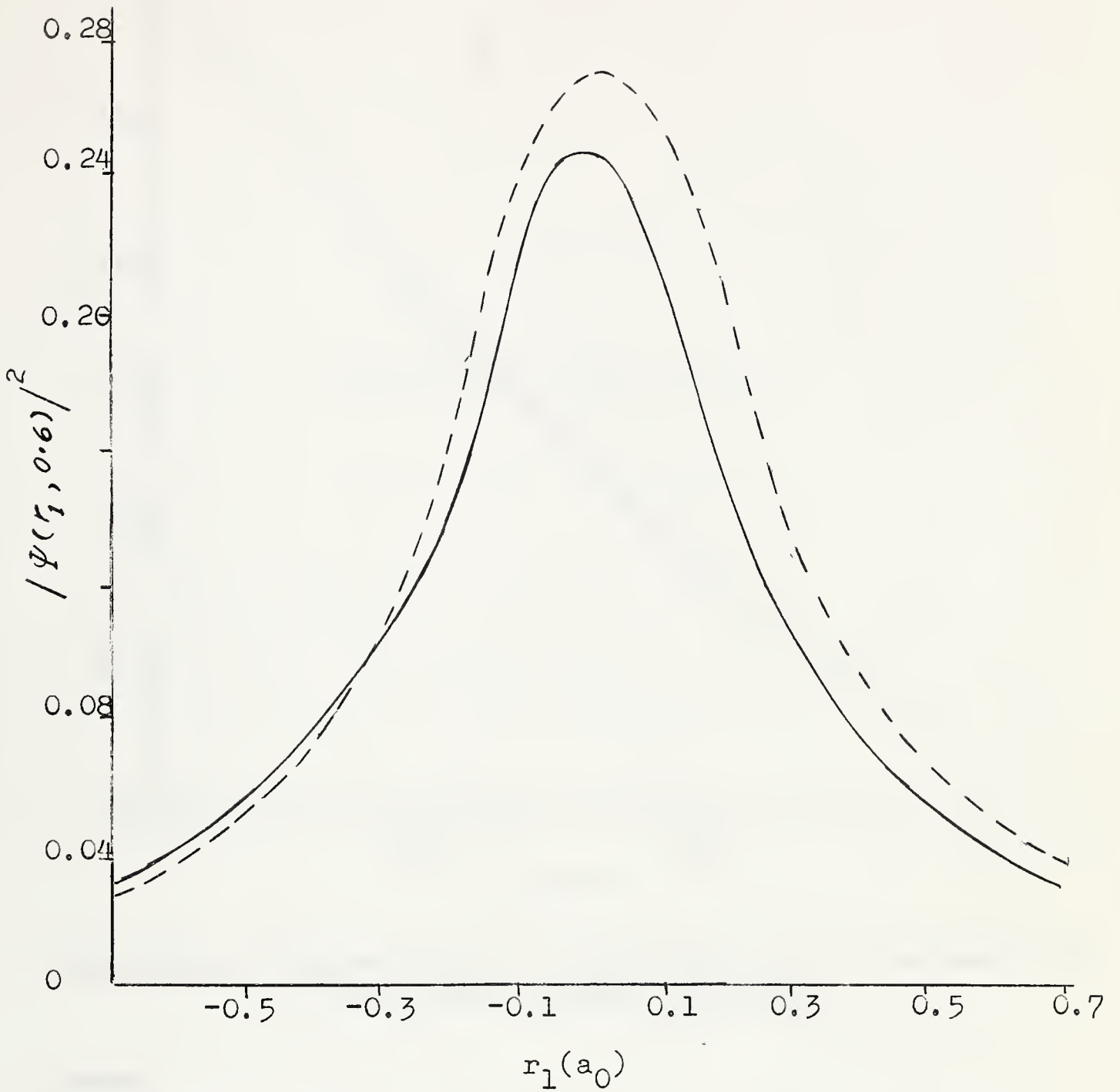


Dependence of χ upon the interelectron distance r_{12}

Legend:

- I Hartree and Ingman
- II Gaussian
- III Roothaan and Weiss

Figure 5



Comparison of the probability distribution

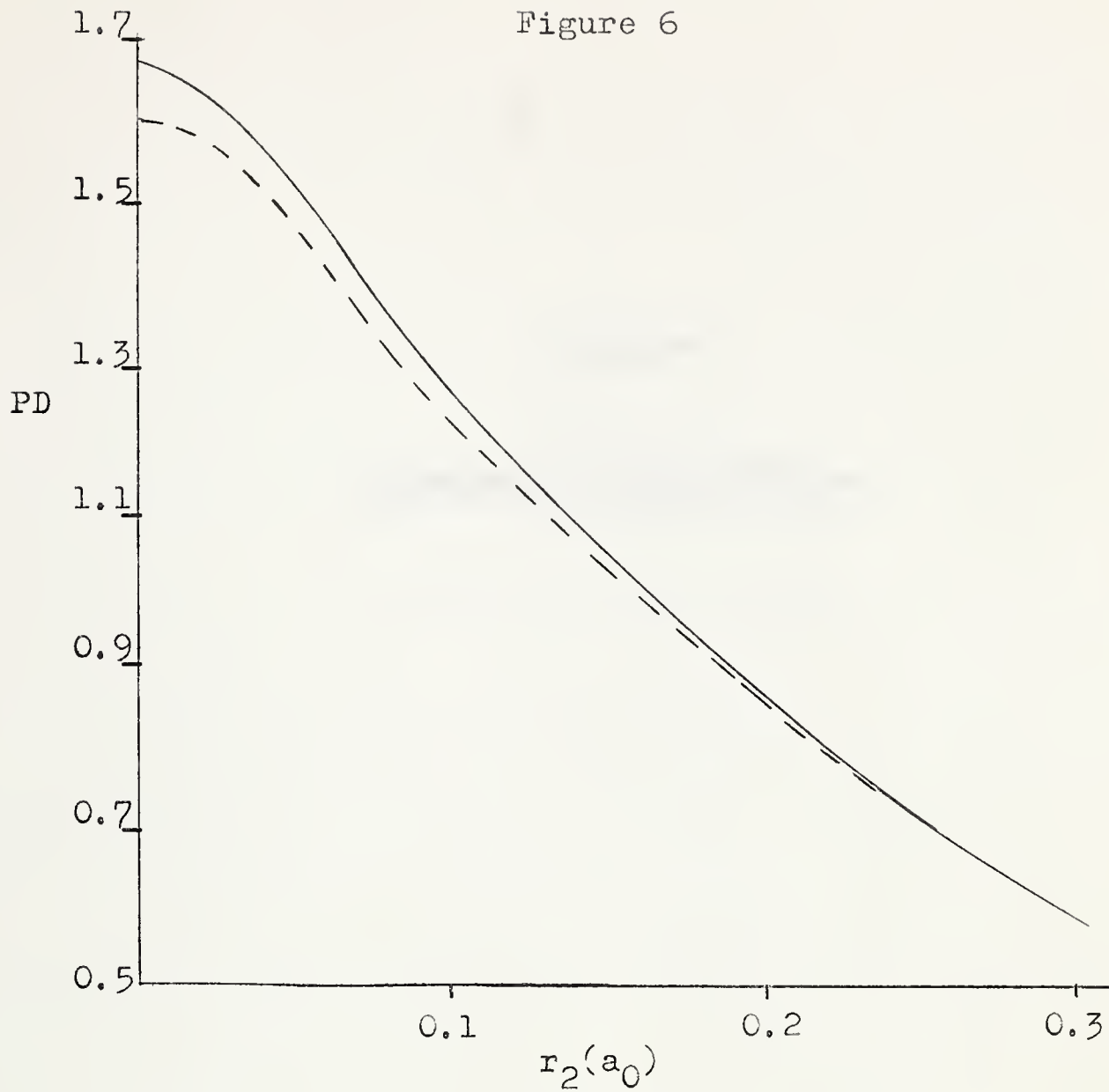
$$/\Psi(r_1, 0.6)/^2$$

for the correlated and non-correlated function

Legend:

Correlated $p = 3, q = 2$ - - - - -

Non-correlated $p = 3$ _____



Comparison of point density distribution for correlated and
and non-correlated functions

Legend:

Correlated $p = 6, q = 2$ _____

Non-correlated $p = 6$ - - - - -

PART TWO

OPEN-SHELL CONFIGURATIONS

CHAPTER III

THE GENERAL SCF THEORY

III-1 Introduction

The determination of the electronic energy by a variational calculation has been restricted to those systems that the available SCF formalism was capable of handling - namely closed-shell and some open shell configurations^{15,16}. As a result the energies of open-shell systems have been approximated by calculations upon the nearest tractible form. For example, the ionization potential has been approximated by the energy of the highest occupied orbital in the parent closed-shell ground state; even some attempts at describing excited states have been made by the use of the virtual (non-occupied in the ground state) orbitals.

Recently more general methods have been advanced, in particular Huzinaga's¹⁷ method in which a SCF improvement of one orbital at a time is carried out, and that of Birss and Fraga¹⁸ which formulates the SCF problem for a simultaneous variation of all orbitals.

Much of the next three chapters is dependent upon the latter authors' SCF formulation and a resumé of their approach with the pertinent equations follows.

III-2 The General SCF Equations

A separation on the basis of symmetry designation is made at the outset which allows the energy to be written as a sum of two parts: the first involving orbitals of a

certain species μ and subspecies α ; the second, designated below as $\underline{C}$, containing all terms which do not involve these orbitals. Thus one has equation (4) of the reference as:

$$E = 2\sum_i f_i^\mu H_i^\mu + \sum_i \sum_j f_i^\mu f_j^\nu I_{ij}^{\mu\alpha, \nu\beta} + 2\sum_i \sum_m \sum_\nu \sum_{\beta \neq \alpha} f_i^\mu f_m^\nu I_{im}^{\mu\alpha, \nu\beta} + C$$

with the i, j summations extending over all occupied orbitals of symmetry designation μ, α and the m over all occupied orbitals of representations covered by ν, β . The index β cannot represent α when $\nu \equiv \mu$. The fractional occupancy is represented by f with appropriate super- and sub-scripts.

The $I_{im}^{\mu\alpha, \nu\beta}$ represent combinations of two-electron integrals and are given in the reference as

$$I_{im}^{\mu\alpha, \nu\beta} = 2a_{im}^{\mu, \nu} J_{im}^{\mu\alpha, \nu\beta} - b_{im}^{\mu, \nu} K_{im}^{\mu\alpha, \nu\beta}$$

the $J_{im}^{\mu\alpha, \nu\beta}$ and $K_{im}^{\mu\alpha, \nu\beta}$ being the usual coulomb and exchange integrals

$$J_{im}^{\mu\alpha, \nu\beta} = \langle \varphi_i^\mu(1) \varphi_m^\nu(2) / \frac{1}{r_{12}} / \varphi_i^\mu(1) \varphi_m^\nu(2) \rangle$$

$$K_{im}^{\mu\alpha, \nu\beta} = \langle \varphi_i^\mu(1) \varphi_m^\nu(2) / \frac{1}{r_{12}} / \varphi_m^\nu(1) \varphi_i^\mu(2) \rangle$$

Variation in the orbitals leads to the Hartree-Fock equations

$$F_i^{\mu\alpha} \varphi_i^{\mu\alpha} = \sum_k \varphi_k^{\mu\alpha} \theta_{ki}^{\mu\alpha}$$

where

$$F_i^{\mu\alpha} = f_i^\mu H_i^\mu + \sum_i f_i^\mu f_j^\nu I_{ij}^{\mu\alpha} + \sum_m \sum_\nu \sum_{\beta \neq \alpha} f_i^\mu f_m^\nu I_{im}^{\nu\beta} \quad . \quad \text{III-1}$$

Thence, with the introduction of the coupling operator $R^{\mu\alpha}$, which effectively removes the off-diagonal Lagrangian

multipliers, the set of pseudo-eigenvalue equations

$$R^{\mu\alpha} \varphi_i^{\mu\alpha} = \varphi_i^{\mu\alpha} \theta_{ii}^{\mu\alpha} \quad \text{is obtained.}$$

$$R^{\mu\alpha} = \sum_k r_k^{\mu\alpha} \quad . \quad \text{III-2}$$

$$\begin{aligned} r_k^{\mu\alpha} = & \langle \varphi_k^{\mu\alpha} | \langle \varphi_k^{\mu\alpha} / F_k^{\mu\alpha} \rangle - \sum_l \langle \varphi_k^{\mu\alpha} | \langle \varphi_k^{\mu\alpha} / F_l^{\mu\alpha} / \varphi_l^{\mu\alpha} \rangle \langle \varphi_l^{\mu\alpha} / \\ & + \langle \varphi_k^{\mu\alpha} | \langle \varphi_k^{\mu\alpha} / F_k^{\mu\alpha} / \varphi_k^{\mu\alpha} \rangle \langle \varphi_k^{\mu\alpha} / \\ & - \sum_l \langle \varphi_l^{\mu\alpha} | \langle \varphi_l^{\mu\alpha} / F_l^{\mu\alpha} / \varphi_k^{\mu\alpha} \rangle \langle \varphi_k^{\mu\alpha} / \\ & + F_k^{\mu\alpha} / \varphi_k^{\mu\alpha} \rangle \langle \varphi_k^{\mu\alpha} / \end{aligned} \quad \text{III-3}$$

III-3 The LCAO Representation of the SCF Equations

In a more recent work¹⁹ by the same authors the extension has been made to the Linear Combination of Atomic Orbitals (LCAO) context. The orbitals are expanded in terms of a suitable set of basis functions $\chi_p^{\mu\alpha}$ to give

$$\varphi^{\mu\alpha} = \sum_p \chi_p^{\mu\alpha} c_{pi}^{\mu} = \vec{\chi}^{\mu\alpha} \vec{c}_i^{\mu} \quad \text{where the } \vec{\chi}^{\mu\alpha} \text{ is a row vector whose elements are the basis functions of symmetry designation } \mu\alpha \text{ and } \vec{c}_i^{\mu} \text{ is a column vector with elements } c_{pi}^{\mu}.$$

The matrix representation of the pseudo-eigenvalue equations is then

$$\underline{R}^{\mu\alpha} \vec{c}_i^{\mu} = \underline{\theta}_{ii}^{\mu\alpha} \underline{S}^{\mu\alpha} \vec{c}_i^{\mu} \quad \text{III-4}$$

and the representation of $R^{\mu\alpha}$ is developed in the reference as

$$\underline{R}^{\mu\alpha} = \underline{Z}^{\mu\alpha} + \underline{Z}^{\mu\alpha} +$$

$$\text{with } \underline{Z}^{\mu\alpha} = \underline{U}^{\mu\alpha} \underline{S}^{\mu\alpha} - \underline{S}^{\mu\alpha} \underline{V}^{\mu\alpha} \underline{S}^{\mu\alpha} + \frac{1}{2} \underline{S}^{\mu\alpha} \underline{W}^{\mu\alpha} \underline{S}^{\mu\alpha}$$

$$\text{where } \underline{U}^{\mu\alpha} = \sum_k \underline{U}_{k-k}^{\mu\alpha}; \quad \underline{U}_{-k}^{\mu\alpha} = \underline{F}_{-k}^{\mu\alpha} \underline{D}_{-k}^{\mu}$$

$$\underline{V}^{\mu\alpha} = \underline{D}^{\mu} \underline{U}^{\mu\alpha}$$

$$\underline{W}^{\mu\alpha} = \sum_k \underline{W}_{k-k}^{\mu\alpha}; \quad \underline{W}_{-k}^{\mu\alpha} = \underline{D}_{-k}^{\mu} \underline{U}_{-k}^{\mu\alpha}$$

The $\underline{D}_{-k}^{\mu}$ and $\underline{F}_{-k}^{\mu\alpha}$, are respectively, the density matrix

$$\underline{D}_{-k}^{\mu} = \underline{\vec{C}}_{-k}^{\mu} \underline{\vec{C}}_{-k}^{\mu+} \quad (\text{which may be expanded as the supervectors}$$

$\underline{D}_{-k}^{\mu}$) and the representation of the operator $F^{\mu\alpha}$, equation (III-1), in the basis set.

An element of $\underline{F}_{-k}^{\mu\alpha}$ is given as

$$F_{k, st}^{\mu\alpha} = f_k^{\mu} \left[H_{st}^{\mu\alpha} + \sum_{\nu, \beta} \left[\underline{J}_{st}^{\mu\alpha, \nu\beta} \underline{A}_{-k}^{\nu(\mu)} - \underline{K}_{st}^{\mu\alpha, \nu\beta} \underline{B}_{-k}^{\nu(\mu)} \right] \right]$$

$\underline{J}_{st}^{\mu\alpha, \nu\beta}$ and $\underline{K}_{st}^{\mu\alpha, \nu\beta}$ are supermatrices with elements as defined in the reference as

$$J_{pq, rs}^{\mu\alpha, \nu\beta} = \int \chi_p^{\mu\alpha}(\rho) \chi_q^{\mu\alpha}(\rho) \left(\frac{1}{r_{\rho\sigma}} \right) \chi_r^{\nu\beta}(\sigma) \chi_s^{\nu\beta}(\sigma) dv_{\rho} dv_{\sigma}$$

$$K_{pq, rs}^{\mu\alpha, \nu\beta} = \int \chi_p^{\mu\alpha}(\rho) \chi_r^{\nu\beta}(\rho) \left(\frac{1}{r_{\rho\sigma}} \right) \chi_s^{\nu\beta}(\sigma) \chi_q^{\mu\alpha}(\sigma) dv_{\rho} dv_{\sigma}$$

and $\underline{A}_{-k}^{\nu(\mu)}$ and $\underline{B}_{-k}^{\nu(\mu)}$ are column supervectors defined as

$$\underline{A}_{-k}^{\nu(\mu)} = 2 \sum_m f_m^{\nu} a_{km}^{\mu, \nu} \underline{D}_m^{\nu}$$

$$\underline{B}_{-k}^{\nu(\mu)} = 2 \sum_m f_m^{\nu} b_{km}^{\mu, \nu} \underline{D}_m^{\nu}$$

where the $\underline{m}$ summation extends over all occupied orbitals of symmetry designation $\nu\beta$.

The total energy can then be developed as

$$E = \sum_{i\mu\alpha} (f_i^{\mu} H_i^{\mu\alpha} + e_{ii}^{\mu\alpha}).$$

CHAPTER IV

FEATURES OF THE GENERAL SCF FORMULATION

IV-1 Extension of the Formulation

The definition of the two electron integrals as

$$I_{im}^{\mu\alpha, \nu\beta} = 2a_{im}^{\mu, \nu} J_{im}^{\mu\alpha, \nu\beta} - b_{im}^{\mu, \nu} K_{im}^{\mu\alpha, \nu\beta}$$

was intended by the authors to cover all except Σ states. However, it can be shown to be inadequate for configurations such as the singlet

$$\varphi_1^{\mu\alpha} \varphi_1^{\mu\beta}, \text{ e.g., } {}^1(2P_x, 2P_y).$$

The contribution of the electronic repulsion to the total energy can be written for the ${}^1(2P_x, 2P_y)$ configuration as $E_{Rep} = J^{PxPy} + K^{PxPy}$; there being no contribution from the J^{PxPx} , K^{PxPx} , J^{PyPy} or K^{PyPy} .

Since the $J^{PxPx} \neq J^{PxPy}$ it is clear that the coefficient required (here $a = 0$) for the integral J^{PxPx} is different than that required for the J^{PxPy} . The situation is similar for the K^{PxPx} and K^{PxPy} . Hence the a and b which were superscripted toward symmetry species only, must also be superscripted toward the subspecies.

The corrected definition of $I_{im}^{\mu\alpha, \nu\beta}$ would then read

$$I_{im}^{\mu\alpha, \nu\beta} = 2a_{im}^{\mu\alpha, \nu\beta} J_{im}^{\mu\alpha, \nu\beta} - b_{im}^{\mu\alpha, \nu\beta} K_{im}^{\mu\alpha, \nu\beta}$$

With this definition the derivation as given by Birss and Fraga can proceed unchanged to their final formulation.

IV-2 The Ionization Energy

The ionization energy may be defined as $E_g - E_t$ where E_g and E_t are the total electronic energy of the ground and

ionized states respectively. Koopman's theorem²⁰ approximates $E_g - E_t$ by the orbital energy of the electron removed, on the assumption that the orbitals are unchanged in the ground and ionized states.

The expression for Koopman's theorem for a closed shell ground state in the formalism of Birss and Fraga may be readily found by properly relating some of their formulae to earlier work.

Roothaan¹⁶ formulates the total energy for a closed shell as $E(F) = \sum_i \sum_{\mu} \sum_{\alpha} (H_i^{\mu\alpha} + \epsilon_i^{\mu\alpha})$ where $H_i^{\mu\alpha}(1) = \langle \varphi_i^{\mu\alpha} / H_1 / \varphi_i^{\mu\alpha} \rangle$ and $\epsilon_i^{\mu\alpha}$, the orbital energy, is given by $F_i^{\mu} \varphi_i^{\mu\alpha} = \varphi_i^{\mu\alpha} \epsilon_i^{\mu\alpha}$.

From the equation (24) of reference (18) one has for the closed shell that

$$R^{\mu\alpha} \varphi_i^{\mu\alpha} = F_i^{\mu} \varphi_i^{\mu\alpha} = \epsilon_i^{\mu} \varphi_i^{\mu\alpha}. \text{ But } R \varphi_i^{\mu\alpha} = \theta_{ii}^{\mu\alpha} \varphi_i^{\mu\alpha} \text{ so that } \epsilon_i^{\mu\alpha} = \theta_{ii}^{\mu} \text{ for the closed shell.}$$

Equation (III-5) for the total energy then becomes

$$E(R) = \sum_i \sum_{\mu} \sum_{\alpha} (\theta_{ii}^{\mu\alpha} + H_i^{\mu\alpha}) = \sum_i \sum_{\mu} \sum_{\alpha} (\epsilon_i^{\mu} + H_i^{\mu\alpha})$$

One then obtains $E(R) = E(F)$, as one must; an explicit statement (not given by the authors) that the total energies by the two methods are identical for the closed shell.

When the orbitals of the ground and ionized states are the same, Roothaan¹⁵ has shown that $E_g(F) - \epsilon_v = E_t(F)$.

Since $E_g(F) = E_g(R)$ and $\epsilon_v = \theta_v$ for a closed shell one obtains $E_g(R) - \theta_v = E_t(F)$. But $E_g(R) - \theta_v = E_t(R)$ and

hence $E_t(R) = E_t(F)$. Thus $E_g(F) - E_t(F) = \epsilon_v$ and $E_g(R) - E_t(R) = \epsilon_v$ are identical statements and the latter may be taken as the statement of Koopman's Theorem for a closed shell in the formalism of the $\underline{R}$ operator.

The expression of $E_g - E_t$, in terms of ground state quantities, where either or both of the ground and ionized states are open-shell configurations can not be shown in general without explicit reference to the spin states involved.

This can be seen quite readily for, if the energies are written as in equation (4) of reference (18), terms such as $f_{ig}^\mu f_{im}^\nu I_{img}^{\mu\alpha, \nu\beta} - f_{it}^\mu f_{mt}^\nu I_{imt}^{\mu\alpha, \nu\beta}$ will occur. Expanding the integrals gives

$$f_{ig}^\mu f_{mg}^\nu (2a_{img}^{\mu\alpha, \nu\beta} J_{im}^{\mu\alpha, \nu\beta} - b_{img}^{\mu\alpha, \nu\beta} K_{im}^{\mu\alpha, \nu\beta}) \\ - f_{it}^\mu f_{mt}^\nu (2a_{imt}^{\mu\alpha, \nu\beta} J_{im}^{\mu\alpha, \nu\beta} - b_{imt}^{\mu\alpha, \nu\beta} K_{imt}^{\mu\alpha, \nu\beta})$$

In general, to express this difference in terms of ground state parameters only, it would be necessary to relate the ionized state $\underline{a}$'s, $\underline{b}$'s and $\underline{f}$'s to those of the ground state. Such a general relation can be simply found for the $\underline{f}$'s because they are independent of spin states. On the other hand the relation of the sets of $\underline{a}$'s and $\underline{b}$'s for ground and ionized states is highly dependent upon the spin character of both states. For example, compare the parameters required for the description of the 4S and 2P states arising from the ionization of the common 3P ground state of the

carbon atom. The relation between the $\underline{f}$'s of the ground and ionized states is identical for these cases, whereas that between the sets of $\underline{a}$'s and $\underline{b}$'s cannot be simply generalized. Hence, it is suggested that a demonstration of the equality $E_g - E_t = \eta_v$, as an expression of Koopman's theorem, be undertaken in the context of the particular case considered.

One such case which is considered in Chapter V is that of $\text{Li} - \text{Li}^+$. Here

$$E_g = 2 \sum_{i=1}^2 f_i H_i + \sum_{i=1}^2 \sum_{j=1}^2 f_i f_j I_{ij} = 2H_1 + H_2 + I_{11} + I_{12} + \frac{1}{4} I_{22}$$

$$E_t = \sum_{i=1}^1 f_i H_i + \sum_{i=1}^1 \sum_{j=1}^1 f_i f_j I_{ij} = 2H_1 + I_{11} \quad \text{so that}$$

$$E_g - E_t = H_2 + I_{12} \quad \text{where } I_{22} \text{ has been set to zero.}$$

$$\eta_v = \langle \varphi_2 / \frac{F_2}{f_2} / \varphi_2 \rangle = \langle \varphi_2 / H + I_1 / \varphi_2 \rangle = H_2 + I_{12} \quad \text{and one}$$

$$\text{obtains } E_g - E_t = \eta_v.$$

IV-3 Virtual Orbital Energies

The virtual orbital energies for the closed shell formalism of Roothaan could be used in the calculation of excitation energies assuming the other orbitals are the same in the ground and excited states. However, it can be shown that this application is possible only for particular cases in the formalism of the general SCF treatment.

In equations(III-2, III-3) the $\underline{k}, \underline{l}$ refer to occupied orbitals and the summation, of course, extends over occupied orbitals only and in fact the development of section III-1

makes no mention of unoccupied orbitals. However, in the LCAO context occupied and unoccupied orbitals can be obtained and whether occupied or not all must be orthogonal.

Letting $\varphi_m^{\mu\alpha}$ be a non-occupied orbital one has that

$$\begin{aligned} R \varphi_m^{\mu\alpha} &= \sum_k r_k^{\mu\alpha} \varphi_m^{\mu\alpha} \\ &= \sum_k [\varphi_k^{\mu\alpha} \langle \varphi_k^{\mu\alpha} / F_k^{\mu\alpha} / \varphi_m^{\mu\alpha} \rangle - \sum_l \varphi_l^{\mu\alpha} \langle \varphi_k^{\mu\alpha} / F_l^{\mu\alpha} / \varphi_l^{\mu\alpha} \rangle \\ &\quad \times \langle \varphi_l^{\mu\alpha} / \varphi_m^{\mu\alpha} \rangle + \varphi_k^{\mu\alpha} \langle \varphi_k^{\mu\alpha} / F_k^{\mu\alpha} / \varphi_k^{\mu\alpha} \rangle \langle \varphi_k^{\mu\alpha} / \varphi_m^{\mu\alpha} \rangle \\ &\quad - \sum_l \varphi_l^{\mu\alpha} \langle \varphi_l^{\mu\alpha} / F_l^{\mu\alpha} / \varphi_k^{\mu\alpha} \rangle \langle \varphi_k^{\mu\alpha} / \varphi_m^{\mu\alpha} \rangle + F_k^{\mu\alpha} / \varphi_k^{\mu\alpha} \langle \varphi_k^{\mu\alpha} / \varphi_m^{\mu\alpha} \rangle] \end{aligned}$$

Because of the range of the summation, $k \neq m$, and by virtue of orthogonality $\langle \varphi_k^{\mu\alpha} / \varphi_m^{\mu\alpha} \rangle = 0$. The equation reduces to $R \varphi_m^{\mu\alpha} = \sum_k \varphi_k^{\mu\alpha} \langle \varphi_k^{\mu\alpha} / F_k^{\mu\alpha} / \varphi_m^{\mu\alpha} \rangle$.

Multiplying on the left by the bra $\langle \varphi_m^{\mu\alpha} /$ gives

$$\langle \varphi_m^{\mu\alpha} / R \varphi_m^{\mu\alpha} \rangle = \sum_k \langle \varphi_m^{\mu\alpha} / \varphi_k^{\mu\alpha} \rangle \langle \varphi_k^{\mu\alpha} / F_k^{\mu\alpha} / \varphi_m^{\mu\alpha} \rangle.$$

Again $\langle \varphi_m^{\mu\alpha} / \varphi_k^{\mu\alpha} \rangle = 0$, and the right hand side is zero giving

$$\langle \varphi_m^{\mu\alpha} / R \varphi_m^{\mu\alpha} \rangle = 0$$

But $\langle \varphi_m^{\mu\alpha} / R \varphi_m^{\mu\alpha} \rangle = \epsilon_{mm}^{\mu\alpha}$ so that the $\epsilon_{mm}^{\mu\alpha}$ for the unoccupied orbitals have a value zero simply on grounds of orthogonality and hence cannot be considered as orbital energies.

Virtual orbital energies, although unobtainable as the eigenvalues of the $R^{\mu\alpha}$ operator, may be found for certain cases by the use of the $F_i^{\mu\alpha}$ operators which occur in the formulation of the $R^{\mu\alpha}$.

For occupied orbitals one has, from equation (24) of

reference (18) that

$$\langle \varphi_i^{\mu\alpha} / R^{\mu\alpha} / \varphi_i^{\mu\alpha} \rangle = \langle \varphi_i^{\mu\alpha} / F_i^{\mu\alpha} / \varphi_i^{\mu\alpha} \rangle = \epsilon_{ii}^{\mu\alpha}$$

i.e. the $\epsilon_{ii}^{\mu\alpha}$ for the occupied orbital $\varphi_i^{\mu\alpha}$ can be obtained with equal validity as the expectation value of $R^{\mu\alpha}$ or $F_i^{\mu\alpha}$. But from the definition of the orbital energy

$$\eta_i^{\mu\alpha} = \epsilon_{ii}^{\mu\alpha} / f_i^{\mu} \quad \text{one has that}$$

$$\eta_i^{\mu\alpha} = \langle \varphi_i^{\mu\alpha} / \frac{F_i^{\mu\alpha}}{f_i^{\mu}} / \varphi_i^{\mu\alpha} \rangle$$

Taking the definition of the virtual orbital energy to mean the expectation value for the virtual orbital of that operator which may be used to evaluate the occupied orbital energies, one obtains

$$\langle \varphi_m^{\mu\alpha} / \frac{F_i^{\mu\alpha}}{f_i^{\mu}} / \varphi_m^{\mu\alpha} \rangle = \eta_{mm}^{\mu\alpha}$$

as the virtual orbital energy. The problem then is to choose the $\frac{F_i^{\mu\alpha}}{f_i^{\mu}}$.

In closed-shell configurations all the $F_i^{\mu\alpha}$ are the same. Even in some open-shell configurations the $F_i^{\mu\alpha}$ may be the same for a given symmetry designation (e.g. $(1S)^1(2S)^1(2P)^n$). The proper operator is immediately obtained in both cases. However in situations where the $F_i^{\mu\alpha}$ are different, the selection of the proper operator cannot be made unless some further step is taken such as using an $F_i^{\mu\alpha}$ averaged within that symmetry species.

CHAPTER V

ATOMIC APPLICATIONS

V-1 Introduction

As indicated earlier, properties of open-shell configurations have been obtained from calculations upon the nearest closed-shell configuration. The basic approximation involved here is that the orbitals in the open- and closed-shell will not in fact differ appreciably and may be taken to be the same (this will be referred to as "constancy of orbitals"). Since the formalism for open-shell configurations is now available it is possible to test the adequacy of this approximation.

In this chapter the approximation will be tested in the atomic systems; He^+ , He ; Li^+ , Li ; Be^+ , Be , by comparing the orbitals found for the ground and the ionized states and by comparing the derived quantity, the ionization energy, as given by the approximation and by the proper calculation.

V-2 The Wave Functions

The total wave function is given by an antisymmetrized product of one electron functions $\Psi = A \prod_{i=1}^n \varphi_i$ where the φ_i are given as expansions in Slater-type functions of spherical symmetry

$$\varphi_i(r) = \sum_s c_{is} \chi_s \text{ where } \chi_s = N_s r^{s-1} \exp[-Z_s r].$$

N is the normalization constant,

$$N_s = \left[\frac{(2Z_s)^{2s+1}}{4\pi (2s!)} \right]^{1/2}$$

The orbital exponent Z_s was evaluated using Slater's rules²¹ as a guide. The values selected for these systems are shown in the table below.

System	s	- Z -		
		1	2	3
He		2.000	0.575	0.100
Li		2.700	0.650	0.300
Be		3.700	0.975	0.300

V-3 The Integrals and the SCF Solution

The one-electron integrals*, H_{rs} , required, can be formulated by standard methods¹² to give

$$H_{rs} = \frac{sZ_r^2 + rZ_s^2 - (sZ_r - rZ_s)^2}{2(r + s - 1)(r + s)} S'_{rs}$$

$$\text{where } S'_{rs} = 4\pi N_r N_s \left[\frac{(r + s)!}{(Z_r + Z_s)^{r + s + 1}} \right]$$

The two-electron integrals* were derived by successive differentiation of an expression for the simplest integral (i.e. $\langle \chi_1^{(1)} \chi_1^{(1)} / \frac{1}{r_{12}} / \chi_1^{(2)} \chi_1^{(2)} \rangle = \langle \varphi_{k1} \varphi_{k2} / \frac{1}{r_{12}} / \varphi_{k3} \varphi_{k4} \rangle$)

Barnett and Coulson give

$$\langle \varphi_{k1} \varphi_{k2} / \frac{1}{r_{12}} / \varphi_{k3} \varphi_{k4} \rangle = (K_1^3 K_2^3 K_3^3 K_4^3)^{1/2} K_a^{-3} K_b^{-2} (1 - 2\nu^2 + \nu^3)$$

where the K_s are the orbital exponents Z_s and

$$K_a = \frac{K_1 + K_2}{2}$$

*The one-electron and two-electron integrals and a program to calculate them were developed by Mr. R.E.D. McClung for another problem and were adopted for the purposes of this section.

$$K_b = \frac{K_3 + K_4}{2}$$

$$\nu = \frac{K_b}{K_a + K_b}$$

Algebraic manipulation of these equalities allows the integral to be cast in the more convenient form as

$$\langle \chi_1^{(1)} \chi_1^{(1)} / \frac{1}{r_{12}} / \chi_1^{(1)} \chi_1^{(1)} \rangle = \pi^2 N_1 N_2 N_3 N_4 \\ \times \left[\frac{K_a^2 + 3K_a K_b + K_b^2}{K_a^2 K_b^2 (K_a + K_b)^3} \right]^2$$

If it is noted that $\frac{\partial}{\partial Z_i} r^{i-1} e^{-Z_i r} = -r^i e^{-Z_i r}$, then the

integral $\langle \chi_p^{(1)} \chi_q^{(1)} / \frac{1}{r_{12}} / \chi_r^{(2)} \chi_s^{(2)} \rangle$ can be derived from

the above formula as

$$\langle \chi_p^{(1)} \chi_q^{(1)} / \frac{1}{r_{12}} / \chi_r^{(1)} \chi_s^{(2)} \rangle = \pi^2 2^{-(p+q+r+s-4)} N_p N_q N_r N_s \\ \times \frac{\partial^{p+q-2}}{\partial K_a^{p+q-2}} \left[\frac{\partial^{r+s-2}}{\partial K_b^{r+s-2}} \left[\frac{K_a^2 + 3K_a K_b + K_b^2}{K_a^2 K_b^2 (K_a + K_b)^3} \right] \right]$$

A program* to calculate these integrals was available for the IBM 1620. A master program was constructed which formulated the matrix representation of the pseudo-eigenvalue equations (III-4) for both the ground and ionized states and solved the matrix equations in a manner similar to that of section I-7.

*See footnote previous page.

V-4 Results and Discussion

The calculated total energies, ionization energy, highest occupied orbital energy and experimental ionization energy are shown in Table VII. The difference between the ionization energies as given by $E_g - E_t$ and by ϵ_v , the orbital energy, is tabulated in the sixth column of the table. The percentage contribution of the experimental ionization energy to the total energy is given in the last column. The SCF coefficients for the ground and ionized state are displayed in Table VIII.

A comparison of the orbitals for the ground and ionized states in the three systems, shows quite clearly that the constancy of the orbitals becomes progressively better from He to Li to Be. The degree of constancy is parallel to the contribution of the electron to be ionized to the total energy, as displayed in the last column of the table. Thus in helium, where the orbitals differ noticeably, the ionization energy is 33% of the total whereas in beryllium, where the orbitals are very similar, the ionization energy is 2%. Hence it appears that the approximation will become more accurate the larger the atomic system and in fact even with a system as small as beryllium the approximation is already quite good.

A comparison of the derived quantity, the ionization energy, indicates that the change in its value as given by the two methods is some 5% in helium, 2% in lithium and 1%

in beryllium. This trend is, of course, consistent with the observations above and indicates that the orbitals, even with the small beryllium system are sufficiently constant that a derived quantity such as the ionization energy is given to quite good accuracy by the closed-shell calculation.

TABLE VII

Constancy of the derived ionization energy.

System	Electronic Energy (au.)	Ionization Energies (au.)				$\frac{\epsilon_v}{E_g}$ %
		$E_g - E_t$	ϵ_v	Expt.	$E_g - E_t - \epsilon_v$	
He ⁺	-2.000					
		-0.787		-0.903	0.037	33
He	-2.787		-0.824			
Li ⁺	-7.224					
		-0.194		-0.198	0.004	3
Li	-7.418		-0.198			
Be ⁺	-14.247					
		-0.309		-0.342	0.003	2
Be	-14.556		-0.312			

TABLE VIII

Coefficients for the occupied orbitals.

System	C_1	C_2	C_3
He ⁺	1.00	0.00	0.00
He	0.95	0.16	0.01
Li ⁺	1.00	-0.02	-0.01
Li	1.01 -0.12	-0.04 1.02	-0.01 0.00
Be ⁺	1.00 -0.18	-0.02 1.03	0.00 -0.04
Be	1.00 -0.20	-0.01 1.02	0.00 -0.02

CHAPTER VI

MOLECULAR APPLICATIONS

VI-1 Introduction

In theory it would be possible to carry out a procedure exactly as in the last chapter to test the constancy of the orbitals for large polyatomic molecules. In practice this is not so for the complexity of the problem forces the introduction of further approximations. Clearly it is necessary to show that the method of testing is either independent of these additional approximations or at least still reliable in spite of them.

Certain of the approximations of the Pariser-Parr method are investigated below and numerical tests carried out on the systems of the previous chapter to determine the implications of the approximations upon the testing method. Having established that the test method is reliable within a context similar to that of the Pariser-Parr method an investigation of the constancy of the orbitals is carried out for some molecular systems.

VI-2 The Approximation of Orthogonal Basis Functions

In the Pariser-Parr method approximations are made, the effects of which are difficult to investigate analytically. However, the approximation of orthogonal basis functions can be discussed to some extent and although justifications²⁵ for this assumption can be given, it can be readily shown that a true Hartree-Fock SCF LCAO MO calculation is not being performed.

A set of non-orthonormal basis functions χ_r may be employed to obtain the integrals H_{rs} , J_{pqrs} , K_{pqrs} and thence the representation of the Hartree-Fock operator,

$$\underline{R} \vec{c} = \underline{\theta} \underline{S} \vec{c} \quad \text{VI-5}$$

or, for the closed-shell in the equivalent form given by Roothaan¹⁵,

$$\underline{F} \vec{c} = \underline{\epsilon} \underline{S} \vec{c} \quad \text{VI-6}$$

If the basis functions χ_r are now taken to be orthogonal and the same basic integrals retained in the formation of the representation of $\underline{F}$ one has

$$\underline{F} \vec{c} = \underline{\epsilon} \vec{c} \quad \text{VI-7}$$

Equations (VI-6) and (VI-7) would be equivalent if

$\underline{m}^+ \underline{F} \underline{m} = \underline{F}$; here $\underline{m}$ is determined by

$$\underline{m}^+ \underline{S} \underline{m} = \underline{I} \quad \text{VI-8}$$

Roothaan has shown that $\underline{F}$ is invariant only under a unitary transformation. But equation (VI-8) can be rewritten as $\underline{S} = (\underline{m}^+)^{-1} \underline{m}^{-1} = (\underline{m} \underline{m}^+)^{-1}$, which becomes, if $\underline{m}$ is unitary $\underline{S} = (\underline{I})^{-1} = \underline{I}$. Hence if $\underline{m}$ is to be unitary then $\underline{S}$ must be a unit matrix. Thus the matrix $\underline{F}$ is invariant under the transformation only if the basis functions upon which it is based were orthogonal. Thus in equation (VI-7) $\underline{F}$ is not the representation of the Hartree-Fock operator.

It should be emphasized that although a Hartree-Fock SCF energy is not found a variation treatment can be carried out and a minimum value obtained.

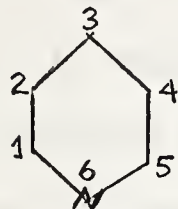
VI-3 Implications

The implications of the above result were investigated by arbitrarily setting $\underline{S} = \underline{I}$ in the representation of the He, He⁺, Li, Li⁺, Be, Be⁺ systems as given in section V-3. The SCF values of the total electronic "energies" for the ground and ionized states as well as values for the ionization energy for the various methods of formation are given in Table X. A comparison of the orbitals as given in Table IX shows that the constancy of the orbitals for the ground and ionized states is approximately the same as for the correct calculation of Chapter V. The quantities in the last column of Table X exhibit the same trend as that of column six of Table VII, indicating that the magnitude of the difference in the ionization energy should be very close to that obtained with a proper calculation. It may be concluded that although the total energy is no longer reliable, comparison between the ground and ionized states, which is the basis of the test method, is still reliable.

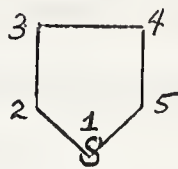
VI-4 Application

Since the method of testing appears to be reliable, even though $\underline{S}$ is arbitrarily set to $\underline{I}$, an investigation was carried out to test the constancy of the orbitals in systems where the full Pariser-Parr treatment is involved. The pyridine, thiophene and isothiazole molecules were chosen as typical systems.

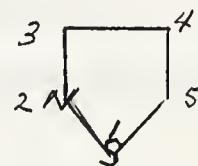
The molecular orbitals were expanded in terms of symmetry basis functions which could be linear combinations of atomic 2P orbitals. For the numbering of centers below



Pyridine



Thiophene



Isothiazole

one obtains basis functions for the symmetry designation A and B as:

For pyridine:

$$\chi_1^A = 2^{-1/2} (2P_{1z} + 2P_{5z}); \chi_2^A = 2^{-1/2} (2P_{2z} + 2P_{4z})$$

$$\chi_3^A = 2P_{3z}; \chi_4^A = 2P_{6z}$$

$$\chi_1^B = 2^{-1/2} (2P_{1z} - 2P_{5z}); \chi_2^B = 2^{-1/2} (2P_{2z} - 2P_{4z})$$

For thiophene:

$$\chi_1^A = 2P_{1z}; \chi_2^A = 2^{-1/2} (2P_{2z} + 2P_{5z}); \chi_3^A = 2^{-1/2} (2P_{3z} + 2P_{4z})$$

$$\chi_1^B = 2^{-1/2} (2P_{2z} - 2P_{5z}); \chi_2^B = 2^{-1/2} (2P_{3z} - 2P_{4z})$$

For Isothiazole:

$$\chi_1^A = 2P_{1z}; \chi_2^A = 2P_{2z}; \chi_3^A = 2P_{3z}; \chi_4^A = 2P_{4z}$$

$$\chi_5^A = 2P_{5z}$$

The integrals for these basis functions were calculated in terms of the atomic integrals tabulated in Tables XI and XII.

The values given for these integrals were calculated from data given in the literature²⁴ and that these may or may not be the best values for the integrals is not in question. It is sufficient for our purpose that representations of the operator $\underline{R}$ be obtained which are typical of those obtained in Pariser-Parr calculations.

The representation of the $\underline{R}$ operator for both the ionized and parent ground state was formulated and the pseudo-eigenvalue equations solved for the SCF solutions in a manner similar to that of section I-7.

As indicated by the results of the previous chapter the total energies may not be meaningful. Table XIII shows the orbitals of the ground and ionized states and Table XIV displays the ionization energies given by $E_g - E_t$ and by the energy, ϵ_v , of the highest occupied orbital. Again it is clear that the orbitals change very little and the approximation of open-shell quantities by those from a neighbouring closed shell appears quite good for large molecules.

Table IX

Coefficients for the orbitals in the
arbitrary S matrix calculations.

System	c_1	c_2	c_3
He ⁺	0.96	0.27	0.00
He	0.93	0.37	0.00
Li ⁺	0.98	0.21	0.02
Li	0.97	0.25	0.04
	-0.24	0.83	0.50
Be ⁺	0.98	0.18	0.00
	-0.18	0.95	0.24
Be	0.98	0.20	0.00
	-0.19	0.94	0.28

Table X

Arbitrary S matrix calculations.

Systems	Total Electronic Energy (au.)		Ionization energy (au.)		
	Calculated	Experimental	$E_g - E_t$	ϵ_v	$E_g - E_t - \epsilon_v$
He ⁺	-2.125	-2.000			
			-.903		0.026
He	-2.980	-2.903		-0.877	
Li ⁺	-7.437	-7.280			
			-0.185		-0.103
Li	-7.622	-7.478		-0.198	
Be ⁺	-14.725	-14.327			
			-0.275		0.004
Be	-15.000	-14.669		-0.271	

Table XI

Two-electron repulsion integrals*.

Pyridine					
10.5	7.30	5.46	4.90	5.46	7.68
	10.5	7.30	5.46	4.90	5.60
		10.5	7.30	5.46	4.97
			10.5	7.30	5.60
				10.5	7.68
					12.30
Thiophene					
11.90	6.58	4.90	4.90	6.58	
	11.08	7.51	5.63	5.39	
		11.08	7.40	5.63	
			11.08	7.51	
				11.08	
Isothiazole					
11.90	7.09	4.90	4.90	6.58	
	12.74	7.81	5.72	5.46	
		11.08	7.40	5.63	
			11.08	7.51	
				11.08	

*The integrals are displayed in a compressed matrix array

$$I_{ij} = \int 2P_i(1) 2P_i(1) \frac{1}{r_{12}} 2P_j(2) 2P_j(2) d\tau$$

where the subscripts refer to atomic centers. The integral values are quoted in ev. for ready comparison to the literature.

Table XII

Core integrals*.

Pyridine					
42.02	2.40	--	--	--	2.58
	41.78	2.40	--	--	--
		41.71	2.40	--	--
			41.78	2.40	--
				42.02	2.58
					46.04
Thiophene					
45.85	3.00	--	--	3.00	
	43.24	2.66	--	--	
		41.88	2.12	--	
			41.88	2.66	
				43.24	
Isothiazole					
46.34	3.00	--	--	3.00	
	47.50	2.66	--	--	
		42.19	2.12	--	
			41.98	2.66	
				43.31	

*The core integrals are displayed as a compressed matrix

$$C_{ij} = - \int 2P_i(1) H_{core}(1) 2P_j(1) d\tau$$

where the i,j refer to atomic centers. For units see the footnote to the previous table.

Table XIII

Coefficients for the orbitals of the Pariser-Parr calculations.

System	Symmetry	C ₁	C ₂	C ₃	C ₄	C ₅
Pyridine	A	0.57	0.52	0.32	0.53	
	A	-0.27	0.49	0.58	-0.59	
	B	0.69	0.73			
Pyridine Ion	A	0.57	0.49	0.35	0.57	
	A	-0.25	0.51	0.60	-0.56	
	B	0.69	0.72			
Thiophene	A	0.65	0.61	0.44		
	A	-0.61	0.08	0.79		
	B	0.85	0.52			
Thiophene Ion	A	0.65	0.62	0.44		
	A	-0.58	0.04	0.81		
	B	0.87	0.50			
Isothiazole	A	0.62	0.51	0.32	0.30	0.41
	A	-0.11	0.63	0.31	-0.36	-0.61
	A	-0.61	0.02	0.53	0.58	0.06
Isothiazole Ion	A	0.61	0.52	0.31	0.30	0.41
	A	0.11	-0.62	-0.32	0.37	0.61
	A	-0.61	0.02	0.52	0.59	0.06

Table XIV

Ionization energies (au.) for the Pariser-Parr approximation.

System	$E_g - E_t$	ϵ_v	$E_g - E_t - \epsilon_v$
Pyridine	-0.424	-0.424	0.000
Thiophene	-0.394	-0.397	0.003
Isothiazole	-0.401	-0.401	0.000

PART THREE

THE VARIATIONAL APPROACH TO THE DESCRIPTION
OF NMR AND EPR PHENOMENA

CHAPTER VII

IMPLICATIONS OF THE PERTURBATION APPROACH ON THE DESCRIPTION OF NMR AND EPR PHENOMENA

VII-1 Introduction

The structure of the spectra observed by nuclear magnetic resonance (NMR) and electron paramagnetic resonance (EPR) may be ascribed to two sources. The gross structure represents the transitions of the system between two energy levels defined principally by the interaction of the nuclei and electrons with an external field which has been modified by the induced magnetic field of the orbital motion of the electrons. The hyperfine splittings of this structure are considered as arising from the magnetic interactions between the nuclei and electrons of the system.

The interpretation of the hyperfine structure, particularly as given by Ramsey²² and others for NMR, has been hitherto quite successful. Recently, however, experimental observations²³ have been made which are in no way consistent with previous treatments in that they imply negative coupling constants. As a result there has been considerable discussion on the shortcomings of the previous treatments. For example, McLaughlin²⁶ has pointed out the implications of the closure rule as used by McConnell,²⁷ Alexander²⁸ has focused attention on the lack of spin-correlation in Ramsey's approach and Acrivos³⁵ has investigated the effect of the use of molecular orbitals in place of valence bond structures in obtaining the spin-density. However, all such discussions have been within

the context of the perturbation technique as first applied by Ramsey. Even those attempts, for example the variational approach of O'Reilly³², which have departed from the perturbation method have been oriented towards providing a description of the phenomena in terms of concepts introduced by the perturbation method.

This study has investigated the implications of the perturbation approach itself. It is found that the nature of the phenomena is considerably obscured and that a fundamentally different approach is possible in which electron spin and nuclear spin correlation is introduced automatically and the difficulties of the perturbation treatment pointed out in the previous paragraph avoided. In an illustrative system, the equations obtained allow a quite simple analysis of the factors upon which the spin character of the electrons and nuclei are dependent. In a final section the relation of magnetic resonance phenomena to chemical concepts (e.g., electronegativity) is demonstrated quite simply.

VII-2 The Hamiltonian

The total hamiltonian, H_T , for a molecular system in the presence of an external magnetic field²⁹, can be given as

$$H_T = H^1 + H^2 + H^3 + H^c$$

where:

$$H^1 = \sum_k \frac{1}{2m} \left(\frac{\hbar}{i} \nabla_k + \frac{e}{c} \sum_n \hbar \gamma_N \vec{I}_N \times \frac{\vec{r}_{kN}}{r_{kN}^3} \right)^2 + V + H_{LL} + H_{LS} + H_{SS}$$

$$H^2 = 2\beta\hbar \sum_k \sum_N \gamma_N [3(\vec{S}_k \cdot \vec{r}_{kN})(\vec{I}_N \cdot \vec{r}_{kN}) r_{kN}^{-5} - (\vec{S}_k \cdot \vec{I}_N) r_{kN}^{-3}]$$

$$H^3 = \frac{16\pi\beta}{3} \hbar \sum_k \sum_N \gamma_N \delta(\vec{r}_{kN})(\vec{S}_k \cdot \vec{I}_N)$$

$$H^c = \sum_N \gamma_N \vec{H}_N \cdot \vec{I}_N + \sum_k \gamma_k \vec{H}_k \cdot \vec{S}_k$$

H^1 can be expanded as:

$$H^1 = H^0 + H_{LL} + H_{LS} + H_{SS} + H^{1a} + H^{1b}$$

where,

$$H^0 = \sum_k \sum_N \left(-\frac{\hbar^2}{2m} \nabla_k^2 - \frac{1}{r_{kN}} \right) + V$$

$$H^{1a} = \frac{e^2 \hbar^2}{2mc^2} \sum_N \sum_N \sum_k \gamma_N \gamma_N (\vec{I}_N \times \frac{\vec{r}_{kN}}{r_{kN}^3}) \cdot (\vec{I}_N \times \frac{\vec{r}_{k'N'}}{r_{k'N'}^3})$$

$$H^{1b} = \frac{e \hbar^2}{mci} \sum_N \sum_k \gamma_N r_{kN}^{-3} (\vec{I}_N \times \vec{r}_{kN}) \cdot \nabla_k.$$

V is the interelectron coulomb potential, H_{LL} , H_{LS} and H_{SS} are the electron orbital-orbital, spin-orbital and spin-spin interactions respectively. H^{1a} and H^{1b} may be regarded as nuclear spin interactions with the electron orbital motion in that the nuclear magnetic moment induces electron currents in the system which, in turn, set up a secondary magnetic field experienced by other nuclei. H^2 represents the dipole-dipole interactions between the nuclear magnetic moment and electronic magnetic moments. H^3 is the Fermi contact potential for the interaction between the nuclear magnetic moment and the electron spin density at the nucleus. The contribution of the external magnetic field through the term $\vec{H}_N \cdot \vec{I}_N$ in H^c , is the potential energy of the magnetic moment of the nucleus

in the magnetic field about the nucleus. $\vec{H}_k \cdot \vec{S}_k$ is the analogous potential for the electron and the external field.

The terms in the hamiltonian may be grouped in two classes: those which treat of interactions which give rise to magnetic resonance phenomena H^{1a} , H^{1b} , H^2 , H^3 and those which do not. Of the latter H^0 is by far the most important term. For the former group it has been shown that H^3 is the dominant term and is principally responsible for the hyperfine splittings of magnetic resonance phenomena. One may then approximate H_T as $H_T^0 \doteq H^0 + H_{FC} + H^C$ where H_{FC} represents the Fermi contact potential, H^3 .

The relative magnitude of H_{FC} allows the adoption of the perturbation method in calculating its contribution to the energy. Ramsey²² first utilized this technique in developing a scheme for describing the energy levels observed in NMR spectroscopy and latterly the perturbation technique has found ready expression in the description of EPR phenomena. Subsequently a considerable body of material, both theoretical and interpretive, has arisen, all within the context of the perturbation method, which purports to describe NMR and EPR phenomena. Although such efforts have been fruitful and have been generally accepted they can be misleading. In particular, the interpretation of the experimental data of NMR in terms of the coupling constants of Ramsey has been based upon concepts which can be shown to be the consequence of the perturbation technique and not the result of the interactions described by the hamiltonian.

VII-3 Implications of the Perturbation Technique

Because the perturbation technique must be carried to second order to provide the description of systems of interest in NMR the fundamental nature of the phenomena has been considerably obscured, more so than in EPR. Hence a thorough discussion of the implications of the use of the perturbation technique in the description of NMR phenomena is in order.

NMR spectroscopy involves magnetic resonance transitions of molecules in a ground electronic state which is most often a singlet state. If H_{FC} is considered as a perturbation on a singlet ground state wave function, $|0\rangle$ then the first and second order perturbation energies are

$$\delta E^{(1)} = \langle 0 | H_{FC} | 0 \rangle = 0; \quad \delta E^{(2)} = - \sum_{i \neq 0} \frac{\langle 0 | H_{FC} | i \rangle \langle i | H_{FC} | 0 \rangle}{E_i - E_0}$$

where $|0\rangle$, $|1\rangle$, $|i\rangle$, etc., are electronic wave functions for the system (i.e., $|i\rangle$ only contains electronic space and spin variables).

Substitution of the explicit form for H_{FC} gives

$$\delta E^{(2)} = - \left(\frac{16\pi h^2}{3} \right) 2 \sum_k \sum_{\sigma_k} \sum_N \sum_{\sigma_N} \sum_{i \neq 0} \frac{\gamma_N \gamma_N \langle 0 | \delta(\vec{r}_{kN}) \vec{S}_k \cdot \vec{I}_N | i \rangle \langle i | (\delta \vec{r}_{k,N}) \vec{S}_k \cdot \vec{I}_N | 0 \rangle}{E_i - E_0}$$

The integration implied by the bra-ket notation can only be over variables of the bra and ket and thus there will be integration over the electronic coordinates only. Hence

the nuclear spin vectors can be removed from the integration summation. For rapidly tumbling collections of molecular systems, averaging over all orientations gives³⁰

$$E^{(2)} = -\sum_N \sum_{N'} \frac{1}{3} \vec{I}_N \cdot \vec{I}_{N'} \sum_{\mathbf{k}} \sum_{\mathbf{k}'} \sum_{i \neq 0} \left(\frac{16\pi}{3} \frac{h^2}{\dots} \right)^2$$

$$\frac{\langle 0 / \delta \vec{r}_{kN} \vec{S}_k / i \rangle \langle i / \delta \vec{r}_{k'N'} \vec{S}_{k'} / i \rangle}{E_i - E_0}$$

$$= \sum_N \sum_{N'} \vec{I}_N \cdot \vec{I}_{N'} J_{NN'}$$

with $J_{NN'}$, the coupling constant. The resulting form is $\vec{I}_N \cdot \vec{I}_{N'}$, but it is clear that this form is a result of the use of wave functions containing only electron variables coupled with the use of the second order perturbation term.

In the Ramsey approach the operator $\sum_N \sum_{N'} \vec{I}_N \cdot \vec{I}_{N'} J_{NN'}$ now takes the place of H_{FC} and is used to calculate the energy contribution due to the Fermi contact potential with a wave function which contains only nuclear variables, specifically, nuclear spin variables. In the presence of an external magnetic field the perturbation contributions to the energy are now given by the two operators

$$H_{FC}^R = \sum_N \sum_{N'} \vec{I}_N \cdot \vec{I}_{N'} J_{NN'}, \quad \text{and} \quad H^C = \sum_N \gamma_N \vec{H} \cdot \vec{I}_N = \sum_N \gamma_N H_N I_{zN}$$

where the magnetic field $\vec{H}$ is in the negative z direction. The wave functions upon which they act are, for a system containing two nuclei of spin 1/2,

$$|\eta_1\rangle = c_{11}^{\alpha\alpha} + c_{12}^{\alpha\beta} + c_{13}^{\beta\alpha} + c_{14}^{\beta\beta}$$

$$|\eta_2\rangle = c_{21}^{\alpha\alpha} + c_{22}^{\alpha\beta} + c_{23}^{\beta\alpha} + c_{24}^{\beta\beta} \text{ etc.}$$

In order that the representation of H_{FC}^R and H^C be diagonal the c_{ij} must be determined by solving the

$$\text{secular determinant } |H_{mn} - E \delta_{mn}| = 0$$

$$\text{where } H_{mn} = \langle \eta_m / H_{FC}^R + H^C / \eta_n \rangle$$

The results are $|\eta_1\rangle = \alpha\alpha$

$$|\eta_2\rangle = \frac{1}{\sqrt{2}} (\alpha\beta - \beta\alpha)$$

$$|\eta_3\rangle = \frac{1}{\sqrt{2}} (\alpha\beta + \beta\alpha)$$

$$|\eta_4\rangle = \beta\beta$$

These $|\eta_i\rangle$, each of which has a well defined value of $\Sigma_N I_{NZ}$, are the simultaneous nuclear spin eigenfunctions of H^C and H_{FC}^R . The observed transitions of NMR are then taken to be between the $|\eta_i\rangle$. Inspection of the $|\eta_i\rangle$ shows that the transition will be accompanied by a "flipping" of a nucleus from $\alpha \rightarrow \beta$ or $\beta \rightarrow \alpha$ (i.e., $|\eta_1\rangle \rightarrow |\eta_2\rangle$)

It is clear that the foregoing description is a result of the fact that the form of H_{FC}^R allows simultaneous eigenfunctions of H^C and H_{FC}^R to be determined which have well defined values of $\Sigma_N I_{NZ}$ and that this, in turn, leads to a description of the transitions in terms of nuclear "flips". The development has also made it clear that the concept of "nucleus-nucleus coupling", as indicated by the form $\vec{I}_N \cdot \vec{I}_{N'}$, must be more a result of the method than of the interaction, for if one considers the hamiltonian $H_T^O = H_E^O + H_{FC} + H^C$, there are no terms involving the product of two nuclear magnetic moments.

It can also be readily demonstrated that the eigenfunctions of the hamiltonian will not simultaneously have well defined eigenvalues of $\Sigma_N I_{Nz}$. To see this one notes that in order that two operators have simultaneous eigenfunctions they must commute. Writing $A = H^C + H_{FC}$ and $B = \Sigma_N I_{Nz}$.

$$\begin{aligned}
 AB - BA &= \Sigma_N \Sigma_{N'} \Sigma_k [(I_N \cdot S_k) I_{N'z} - I_{N'z} (I_N \cdot S_k)] \\
 &= \Sigma_N \Sigma_{N'} \Sigma_k \Sigma_V (I_{NV} S_{kV} I_{N'z} - I_{N'z} I_{NV} S_{kV}), V = x, y, z. \\
 &= \Sigma_N \Sigma_{N'} \Sigma_k [(I_{NX} S_{kX} I_{N'z} - I_{N'z} I_{NX} S_{kX}) \\
 &\quad + (I_{NY} S_{kY} I_{N'z} - I_{N'z} I_{NY} S_{kY})] \\
 &= \Sigma_N \Sigma_{N'} \Sigma_k [S_{kX} (I_{NX} I_{Nz} - I_{Nz} I_{NX}) \\
 &\quad + S_{kY} (I_{NY} I_{Nz} - I_{Nz} I_{NY})] \\
 &= \Sigma_N \Sigma_k i[-S_{kX} I_{NY} + S_{kY} I_{NX}] \\
 &\neq 0, \quad AB - BA \neq 0
 \end{aligned}$$

Hence A and B do not have simultaneous eigenstates so that the Ramsey perturbation treatment has lead to a concept which describes the true situation incorrectly.

An analysis of the descriptions invoked for EPR would lead to a similar but somewhat less damaging judgement. In EPR unpaired electrons are involved and the doublet electronic spin state can be successfully treated with the first order perturbation term. As a result the principal imperfection has been that the transitions have been

described as "flipping" of electrons - a concept which is invalid on the same grounds as the "flipping" of nuclei.

These comments do not invalidate the perturbation approach but do point out that some of the more common (and one might add, most useful) concepts of NMR and EPR have perhaps achieved a degree of acceptance beyond that necessary and that alternate approaches to the problem could be fruitful.

CHAPTER VIII

DEVELOPMENT OF THE VARIATIONAL DESCRIPTION

VIII-1 The Wave Function

The investigation is carried out within the molecular orbital context where each electron is considered as being described by an orbital function which may extend over the entire system and a spin function is associated with each electron. The description of each nucleus is given by its own particular spin function. The entire system is then described by an antisymmetrized product of the electron orbital, electron spin and nuclear spin functions.

The basic step in the procedure proposed is the recognition that since an electron or nucleus need not be in an eigenstate of S_Z , or I_Z , then the individual electron or nucleus may be in some intermediate state which is a superposition of the possible eigenstates of these operators. This is analogous to Dirac's discussion of the states of polarization of a photon passing through a tourmaline crystal.¹ Let $|\Psi\rangle$ be the state function dependent on all the variables of the system, where $|\Psi\rangle = |A\psi\rangle$, with A an appropriate antisymmetrizer. $|\Psi\rangle = |\Phi\rangle |\eta\rangle$, where $|\Phi\rangle$ is the spin-space function of all the electrons and $|\eta\rangle$ is the spin function of all the nuclei. Let the function $|\Phi\rangle$ be a product of one-electron functions $|\phi_i\rangle = |\psi_i\rangle |\xi_i\rangle$.

The orbital and spin parts of $|\phi_i\rangle$ can be given as the expansion

$$|\psi_i\rangle = \sum_j c_{ij} |\theta_j\rangle$$

$$/\xi_i\rangle = g_{i1}/\sigma_1\rangle + g_{i2}/\sigma_2\rangle ,$$

$/\theta_j\rangle$ is a suitable basis set, $/\sigma_1\rangle$ and $/\sigma_2\rangle$ are the usual spinors, α and β , for the electron. Thus

$$/\phi\rangle = \prod_i^n / \phi_i\rangle = \prod_i^n / \psi_i\rangle / \xi_i\rangle$$

$/\eta\rangle$ is to be a product of functions $/\eta_p\rangle$ where

$$/\eta_p\rangle = \sum_j^s h_{pj} / \rho_j\rangle$$

where the $/\rho_j\rangle$ are the spinors for the nuclei so that

$$/\eta\rangle = \prod_p^q / \eta_p\rangle$$

and hence

$$/\Psi\rangle = \prod_i^n / \psi_i\rangle / \xi_i\rangle \prod_p^q / \eta_p\rangle$$

The nuclei and electrons are non-equivalent particles and so the antisymmetric requirements operate independently on the electrons and the nuclei. Thus there will be an antisymmetrizer for the electrons completely independent of that for the nuclei. The usual approximation that the spatial coordinates of the nuclei remain unchanged will be invoked³³. This in turn means that whether the spatial function of the nuclei is symmetric or antisymmetric will not matter to the energy. This implies that no symmetry requirements can be placed on the nuclear spin function, so that either a symmetric or an antisymmetric nuclear spin function can be employed. Hence in this derivation A will only refer to the electronic antisymmetrizer.

VIII-2 The Variational Equations

There are varying degrees to which a variational calculation may be carried. The most general case will be given by varying the $\underline{c}$, $\underline{g}$ and $\underline{h}$. For the total energy given by

$$E = \frac{\langle \Psi / H_T / \Psi \rangle}{\langle \Psi / \Psi \rangle}$$

the variation in the energy is given by

$$\delta E = 0 = \langle \delta \Psi / H_T / \Psi \rangle - E \langle \delta \Psi / \Psi \rangle \quad \text{VIII-1}$$

where

$$\langle \delta \Psi / = \langle \frac{\partial \Psi}{\partial \phi} / \delta \phi + \langle \frac{\partial \Psi}{\partial \eta} / \delta \eta$$

But the variation in $\langle \phi \rangle$ is independent of the variation in $\langle \eta \rangle$ so that equation (VIII-1) can be written as two equations

$$\delta \phi \left[\langle \frac{\partial \Psi}{\partial \phi} / H_T / \Psi \rangle - E \langle \frac{\partial \Psi}{\partial \phi} / \Psi \rangle \right] = 0 \quad \text{VIII-2}$$

$$\delta \eta \left[\langle \frac{\partial \Psi}{\partial \eta} / H_T / \Psi \rangle - E \langle \frac{\partial \Psi}{\partial \eta} / \Psi \rangle \right] = 0 \quad \text{VIII-3}$$

But since $\phi = \langle \Psi \rangle / \xi$

then

$$\delta \phi \langle \frac{\partial \Psi}{\partial \phi} / = \langle \frac{\partial \Psi}{\partial \psi} / \delta \psi + \langle \frac{\partial \Psi}{\partial \xi} / \delta \xi$$

and equation (VIII-2) can be separated into two equations, since the variations $\delta \psi$ and $\delta \xi$ are independent. One has, finally,

$$\delta \psi \left[\langle \frac{\partial \Psi}{\partial \psi} / H_T / \Psi \rangle - E \langle \frac{\partial \Psi}{\partial \psi} / \Psi \rangle \right] = 0 \quad \text{VIII-4}$$

$$\delta \xi \left[\langle \frac{\partial \Psi}{\partial \xi} / H_T / \Psi \rangle - E \langle \frac{\partial \Psi}{\partial \xi} / \Psi \rangle \right] = 0 \quad \text{VIII-5}$$

For the ψ_i of different symmetry equation VIII-4 can be written as n independent equations

$$\delta\psi_i[\langle \frac{\partial \psi}{\partial \psi_i} / H_T / A\psi \rangle - E \langle \frac{\partial \psi}{\partial \psi_i} / A\psi \rangle] = 0, \quad i = 1, n \quad \text{VIII-6}$$

When certain of the ψ_i are of the same symmetry then not all variations $\delta\psi_i$ are independent and a procedure similar to that of reference (17) or (18) would be required for a variation of the orbitals.

Since no constraints are placed upon the $\langle \xi_i \rangle$ or the $\langle \eta_p \rangle$, equations (VIII-3) and (VIII-5) become

$$\delta\xi_i[\langle \frac{\partial \psi}{\partial \xi_i} / H_T / A\psi \rangle - E \langle \frac{\partial \psi}{\partial \xi_i} / A\psi \rangle] = 0; \quad i = 1, n \quad \text{VIII-7}$$

$$\delta\eta_p[\langle \frac{\partial \psi}{\partial \eta_p} / H_T / A\psi \rangle - E \langle \frac{\partial \psi}{\partial \eta_p} / A\psi \rangle] = 0; \quad p = 1, q \quad \text{VIII-8}$$

The method of section I-4 allows equations (VIII-6, -7, -8) to be written in matrix form

$$\underline{H}^{\emptyset i} \vec{c} = \underline{E}^{\emptyset i} \underline{S}^{\emptyset i} \vec{c} \quad i = 1, n$$

$$\underline{H}^{\xi j} \vec{g}^j = \underline{E}^{\xi j} \underline{S}^{\xi j} \vec{g}^j \quad j = 1, n$$

$$\underline{H}^{\eta p} \vec{h}^p = \underline{E}^{\eta p} \underline{S}^{\eta p} \vec{h}^p \quad p = 1, q$$

where matrix elements similar to those of that section maybe defined. This set of matrix equations maybe taken as the statement of the variational problem for the calculation of all the orbitals, electron spin functions, and nuclear spin functions. No intermediate operator (such as H_{FC}^R) is introduced. No restrictions upon the spin states or spin properties of either the electrons or nuclei are

implied. The orbital and spin functions are to be determined simultaneously to give the minimum energy - the best overall description.

VIII-3 Approximations

The development to this point has been towards a quite general variational treatment for obtaining the lowest energy of H_T . However, the observed energy differences for the hyperfine splittings are of the order of 10^{-16} au. Hence, in order to obtain results of significance, it would be necessary to carry at least 16 figures in all calculations. Such a procedure is by no means impossible with the computational devices available but a less formidable calculation will serve to illustrate the features of the variational approach.

If the first term, H_E^O , in H_T^O is dropped, the hamiltonian becomes simply a sum of the Fermi contact potential and the contribution due to the external field. For an investigation of the hyperfine structure, only the field-independent Fermi contact potential need be considered. The implications of such a rather drastic truncation of the hamiltonian deserve comment.

The central point of the variational method is the calculation of a minimum expectation value for the operator in question. It is quite clear that the minimum of H_T^O would be determined chiefly by H_E^O and so the variational determination of the orbitals would be principally the

result of the effect of H_E^O . Evidently a determination of the orbitals solely on the basis of the operators H_{FC} and H^C would be a rather useless approximation. For this reason, when H_E^O is omitted, as suggested in the above, variation of the ψ_i is omitted and the orbitals used may be determined by H_E^O alone by another method (i.e., the Hartree-Fock LCAO MO's). The form of the energy expression used there will chiefly determine the spin functions of the electrons. They can be only slightly modified by the H_{FC} . Hence if the approximation is to be valid the spin functions determined solely by H_{FC} must be similar to those which would be determined by $H_E^O + H_{FC}$. This can only be done for systems in which H_E^O would determine non-singlet spin functions at the minimum, for the minimum for H_{FC} involves a non-singlet spin function. Since H_E^O only influences the nuclear spin indirectly through the electron spin (the nuclear spin functions are determined chiefly by H_{FC}), it appears that the truncation of the hamiltonian to the single term H_{FC} is reasonable for the variational calculation of the spin functions of the electrons and nuclei in systems which are expected to have non-singlet ground states.

CHAPTER IX

ILLUSTRATION OF THE METHOD

IX-1 The Matrix Representations

As an illustration, the system of two-electrons and two protons was selected.

The orbital functions are then ψ_1 and ψ_2 , with the electron spin functions ξ_1 and ξ_2 and the nuclear spin functions η_1 and η_2 , where:

$$\begin{aligned}\psi_1 &= \sum_i c_i \psi_i & \psi_2 &= \sum_i c_i' \psi_i \\ \xi_1 &= g_1 \alpha + g_2 \beta & \xi_2 &= g_1' \alpha + g_2' \beta \\ \eta_1 &= h_1 \alpha + h_2 \beta & \eta_2 &= h_1' \alpha + h_2' \beta\end{aligned}$$

The truncated form of the hamiltonian discussed in the previous chapter was used. The two orbitals ψ_1 and ψ_2 are considered to be fixed and a variational treatment carried out only on the electron and nuclear spin functions.

The matrix equations to be solved are:

$$\underline{H} \begin{matrix} \xi_1 \\ \underline{g}_m \end{matrix} = \underline{E} \underline{S} \begin{matrix} \xi_1 \\ \underline{g}_m \end{matrix}$$

$$\underline{H} \begin{matrix} \xi_2 \\ \underline{g}_n \end{matrix} = \underline{E} \underline{S} \begin{matrix} \xi_2 \\ \underline{g}_n \end{matrix}$$

$$\underline{H} \begin{matrix} \eta_1 \\ \underline{h}_r \end{matrix} = \underline{E} \underline{S} \begin{matrix} \eta_1 \\ \underline{h}_r \end{matrix}$$

$$\underline{H} \begin{matrix} \eta_2 \\ \underline{h}_s \end{matrix} = \underline{E} \underline{S} \begin{matrix} \eta_2 \\ \underline{h}_s \end{matrix}$$

The total energy matrix $\underline{E}$ is diagonal and the matrices $\underline{H}$ and $\underline{S}$ have the matrix elements given as:

$$H_{mm}^{\xi_1} = \langle \psi_1 \psi_2 \sigma_m \xi_2 \eta_1 \eta_2 / H_{FC} / (\psi_1 \psi_2 \sigma_m \xi_2 - \psi_2 \psi_1 \xi_2 \sigma_m) \eta_1 \eta_2 \rangle$$

$$H_{nn}^{\xi 2} = \langle \psi_1 \psi_2 \xi_1 \sigma_L \eta_1 \eta_2 / H_{FC} / (\psi_1 \psi_2 \xi_1 \sigma_{n'} - \psi_2 \psi_1 \sigma_{n'} \xi_1) \eta_1 \eta_2 \rangle$$

$$H_{rr}^{\eta 1} = \langle \psi_1 \psi_2 \xi_1 \xi_2 \rho_r \eta_2 / H_{FC} / (\psi_1 \psi_2 \xi_1 \xi_2 - \psi_2 \psi_1 \xi_2 \xi_1) \rho_r \eta_2 \rangle$$

$$H_{ss}^{\eta 2} = \langle \psi_1 \psi_2 \xi_1 \xi_2 \eta_1 \rho_s / H_{FC} / (\psi_1 \psi_2 \xi_1 \xi_2 - \psi_2 \psi_1 \xi_2 \xi_1) \eta_1 \rho_s \rangle$$

$$S_{mm}^{\xi 1} = \langle \psi_1 \psi_2 \sigma_m \xi_2 \eta_1 \eta_2 / (\psi_1 \psi_2 \sigma_m \xi_2 - \psi_2 \psi_1 \xi_2 \sigma_m) \eta_1 \eta_2 \rangle$$

$$S_{nn}^{\xi 2} = \langle \psi_1 \psi_2 \xi_1 \sigma_n \eta_1 \eta_2 / (\psi_1 \psi_2 \xi_1 \sigma_{n'} - \psi_2 \psi_1 \sigma_{n'} \xi_1) \eta_1 \eta_2 \rangle$$

$$S_{rr}^{\eta 1} = \langle \psi_1 \psi_2 \xi_1 \xi_2 \rho_r \eta_2 / (\psi_1 \psi_2 \xi_1 \xi_2 - \psi_2 \psi_1 \xi_2 \xi_1) \rho_r \eta_2 \rangle$$

$$S_{ss}^{\eta 2} = \langle \psi_1 \psi_2 \xi_1 \xi_2 \eta_1 \rho_s / (\psi_1 \psi_2 \xi_1 \xi_2 - \psi_2 \psi_1 \xi_2 \xi_1) \eta_1 \rho_s \rangle$$

The integrations implied by the above are carried out in Appendix IV and the matrix elements as developed there are displayed below as:

S matrices:

$$S_{11}^{\xi 1} = (\xi_{22} - s_{12}^2 g_1^n g_1^n) \eta_{11} \eta_{22}$$

$$S_{12}^{\xi 1} = - s_{12}^2 g_1^n g_2^n \eta_{11} \eta_{22}$$

$$S_{22}^{\xi 1} = (\xi_{22} - s_{12}^2 g_2^n g_2^n) \eta_{11} \eta_{22}$$

$$S_{11}^{\xi 2} = (\xi_{11} - s_{12}^2 g_1^m g_1^m) \eta_{11} \eta_{22}$$

$$S_{12}^{\xi 2} = - s_{12}^2 g_1^m g_2^m \eta_{11} \eta_{22}$$

$$S_{22}^{\xi 2} = (\xi_{11} - s_{12}^2 g_2^m g_2^m) \eta_{11} \eta_{22}$$

$\underline{S}^{\eta_1}$

$$S_{11}^{\eta_1} = K^{\eta_1} = S_{22}^{\eta_1}, \quad K^{\eta_1} = (\xi_{22} \xi_{11} - s_{12}^2 \eta_{12}^2) \eta_{22}$$

$$S_{12}^{\eta_1} = 0$$

$\underline{S}^{\eta_2}$

$$S_{11}^{\eta_2} = K^{\eta_2} = S_{22}^{\eta_2}, \quad K^{\eta_2} = (\xi_{22} \xi_{11} - s_{12}^2 \eta_{12}^2) \eta_{11}$$

where $\xi_{nm} = \langle \xi_n / \xi_m \rangle$, $\eta_{rs} = \langle \eta_r / \eta_s \rangle$, $s_{12} = \langle \psi_1 / \psi_2 \rangle$.

H matrices:

$\underline{H}^{\xi 1}$

$$\begin{aligned} H_{11}^{\xi 1} = \frac{\hbar^2}{4} \{ & \xi_{22} [D_A^1 \eta_{22} w_5 + D_B^1 \eta_{11} w_6] + (U_1 [D_A^2 \eta_{22} w_1 \\ & + D_B^2 \eta_{11} w_2] + U_3 [D_A^2 \eta_{22} w_5 + D_B^2 \eta_{11} w_6]) \\ & - 2s_{12} (g_1^n g_1^n [D_A^{12} \eta_{22} w_5 + D_B^{12} \eta_{11} w_6] + g_1^n g_2^n [D_A^{12} \eta_{22} w_1 \\ & + D_B^{12} \eta_{11} w_2]) \} \end{aligned}$$

$$\begin{aligned} H_{12}^{\xi 1} = \frac{\hbar^2}{4} \{ & \xi_{22} [D_A^1 \eta_{22} w_1 + D_B^1 \eta_{11} w_2] - s_{12} [D_A^{12} \eta_{22} w_1 \\ & + D_B^{12} \eta_{11} w_2] \} \end{aligned}$$

$$\begin{aligned} H_{22}^{\xi 1} = \frac{\hbar^2}{4} \{ & -\xi_{22} [D_A^1 \eta_{22} w_5 + D_B^1 \eta_{11} w_6] + (U_1 [D_A^2 \eta_{22} w_1 \\ & + D_B^2 \eta_{11} w_2] + U_3 [D_A^2 \eta_{22} w_5 + D_B^2 \eta_{11} w_6]) \\ & - 2s_{12} (-g_1^n g_1^n [D_A^{12} \eta_{22} w_5 + D_B^{12} \eta_{11} w_6] + g_1^n g_2^n [D_A^{12} \eta_{22} w_1 \\ & + D_B^{12} \eta_{11} w_2]) \} \end{aligned}$$

H ^{$\xi 2$}

$$H_{11}^{\xi 2} = \frac{\hbar^2}{4} \left\{ \xi_{11} [D_A^2 \eta_{22} W_5 + D_B^2 \eta_{11} W_6] + (U_4 [D_A^1 \eta_{22} W_1 + D_B^1 \eta_{11} W_2] + U_6 [D_A^1 \eta_{22} W_5 + D_B^1 \eta_{11} W_6]) - 2S_{12} (g_1^m g_1^m [D_A^{12} \eta_{22} W_5 + D_B^{12} \eta_{11} W_6] + g_1^m g_2^m [D_A^{12} \eta_{22} W_1 + D_B^{12} \eta_{11} W_2]) \right\}$$

$$H_{12}^{\xi 2} = \frac{\hbar^2}{4} \left\{ \xi_{11} [D_A^2 \eta_{22} W_1 + D_B^2 \eta_{11} W_2] - S_{12} [D_A^{12} \eta_{22} W_1 + D_B^{12} \eta_{11} W_2] \right\}$$

$$H_{22}^{\xi 2} = \frac{\hbar^2}{4} \left\{ -\xi_{11} [D_A^2 \eta_{22} W_5 + D_B^2 \eta_{11} W_6] + (U_4 [D_A^1 \eta_{22} W_1 + D_B^1 \eta_{11} W_2] + U_6 [D_A^1 \eta_{22} W_5 + D_B^1 \eta_{11} W_6]) - 2S_{12} (-g_2^m g_2^m [D_A^{12} \eta_{22} W_5 + D_B^{12} \eta_{11} W_6] + g_1^m g_2^m [D_A^{12} \eta_{22} W_1 + D_B^{12} \eta_{11} W_2]) \right\}$$

H ^{η_1}

$$H_{11}^{\eta_1} = \frac{\hbar^2}{4} \left\{ \eta_{22} [D_A^1 \xi_{22} U_6 + D_A^2 \xi_{11} U_3 - 2D_A^{12} S_{12} V_1 V_3] + W_2 [D_B^1 \xi_{22} U_4 + D_B^2 \xi_{11} U_4] + W_6 [D_B^1 \xi_{22} U_6 + D_B^2 \xi_{11} U_3 - 2D_B^{12} S_{12} V_1 V_3] \right\}$$

$$H_{12}^{\eta_1} = \frac{\hbar^2}{4} \eta_{22} [D_A^1 \xi_{22} U_4 + D_A^2 \xi_{11} U_1 - 2D_A^{12} S_{12} V_1 V_2]$$

$$H_{22}^{\eta_1} = \frac{\hbar^2}{4} \left\{ -\eta_{22} [D_A^1 \xi_{22} U_6 + D_A^2 \xi_{11} U_3 - 2D_A^{12} S_{12} V_1 V_3] + W_2 [D_B^1 \xi_{22} U_4 + D_B^2 \xi_{11} U_1 - 2D_B^{12} S_{12} V_1 V_2] \right\}$$

$$\begin{aligned}
& + W_6 [D_B^1 \xi_{22} U_6 + D_B^2 \xi_{11} U_3 - 2D_B^{12} S_{12} V_1 V_3] \} \\
H_{11}^{\eta_2} &= \frac{\hbar^2}{4} \{ \eta_{11} [D_B^1 \xi_{22} U_6 + D_B^2 \xi_{11} U_3 - 2D_B^{12} S_{12} V_1 V_3] \\
& + W_1 [D_A^1 \xi_{22} U_4 + D_A^2 \xi_{11} U_1 - 2D_A^{12} S_{12} V_1 V_2] \\
& + W_5 [D_A^1 \xi_{22} U_6 + D_A^2 \xi_{11} U_3 - 2D_A^{12} S_{12} V_1 V_3] \} \\
H_{12}^{\eta_2} &= \frac{\hbar^2}{4} [\eta_{11} D_B^1 \xi_{22} U_4 + D_B^2 \eta_{11} U_1 - 2D_B^{12} S_{12} V_1 V_2] \\
H_{22}^{\eta_2} &= \frac{\hbar^2}{4} \{ -\eta_{11} [D_B^1 \eta_{22} U_6 + D_B^2 \eta_{11} U_3 - 2D_B^{12} S_{12} V_1 V_3] \\
& + W_1 [D_A^1 \eta_{22} U_4 + D_A^2 \eta_{11} U_1 - 2D_A^{12} S_{12} V_1 V_2] \\
& + W_5 [D_A^1 \eta_{22} U_6 + D_A^2 \eta_{11} U_3 - 2D_A^{12} S_{12} V_1 V_3] \}
\end{aligned}$$

Where the constants of the problem are defined as:

$$D_A^1 = \langle \psi_1 / \delta(r_A) / \psi_1 \rangle \quad ; \quad D_B^1 = \langle \psi_1 / \delta(r_B) / \psi_1 \rangle$$

$$D_A^2 = \langle \psi_2 / \delta(r_A) / \psi_2 \rangle \quad ; \quad D_B^2 = \langle \psi_2 / \delta(r_B) / \psi_2 \rangle$$

$$D_A^{12} = \langle \psi_1 / \delta(r_A) / \psi_2 \rangle \quad ; \quad D_B^{12} = \langle \psi_1 / \delta(r_B) / \psi_2 \rangle$$

The overlap integrals are given by:

$$\xi_{11} = g_1^m g_1^m + g_2^m g_2^m$$

$$\xi_{22} = g_1^n g_1^n + g_2^n g_2^n$$

$$\xi_{12} = v_1^2$$

$$\eta_{11} = h_1^r h_1^r + h_2^r h_2^r$$

$$\eta_{22} = h_1^s h_1^s + h_2^s h_2^s$$

The symbols are explicitly:

$$W_1 = 2h_1^r h_2^r \quad ; \quad W_2 = 2h_1^s h_2^s$$

$$W_5 = h_1^r h_1^r - h_2^r h_2^r \quad ; \quad W_6 = h_1^s h_1^s - h_2^s h_2^s$$

$$U_1 = 2g_1^n g_2^n \quad ; \quad U_4 = 2g_1^m g_2^m$$

$$U_3 = g_1^n g_1^n - g_2^n g_2^n \quad ; \quad U_6 = g_1^m g_1^m - g_2^m g_2^m$$

$$V_1 = g_1^m g_1^n + g_2^m g_2^n \quad ; \quad V_2 = g_1^m g_2^n + g_2^m g_1^n$$

$$V_3 = g_1^m g_1^n - g_2^m g_2^n \quad .$$

IX-2 Analysis of the Matrix Equations

As indicated in the introduction there has been considerable discussion of late on the standard perturbation approaches to NMR and EPR energy levels in view of the disagreement between experiment and theory, with much criticism leveled at the lack of spin correlation, the closure rule, etc. . The approach described earlier has removed those features associated directly with the perturbation technique and an analysis of the resulting equations allows some useful discussion of the source of spin configuration interactions (or spin correlation) in these phenomena.

Spin correlation (or spin configuration interaction)

is usually taken to imply that the spin functions should be given by linear combinations of eigenfunctions of the total spin operator S^2 or I^2 , for example, the spin function for two-electrons would be of the form

$$c_1 [\alpha(1)\alpha(2)] + c_2 [\alpha(1)\beta(2) - \beta(1)\alpha(2)] + \dots$$

$= (g_1\alpha + g_2\beta)(1) + (g_3\alpha + g_4\beta)(2)$, or, in other words, that there be a "mixing" of the α and β spinors. If one considers the off-diagonal elements of the $\underline{H}$ matrices as effecting a mixing of the "states" indicated by diagonal elements, then in the $H^{\xi 1}$ and $H^{\xi 2}$ matrices it is clear that the existence of off-diagonal elements depends on W_1 or W_2 being non-zero. But W_1 and W_2 can be non-zero only if the spin states of the nuclei are mixtures of the two extreme spin states.

Similarly, in the $H^{\eta 1}$ and $H^{\eta 2}$ matrices the mixing due to off-diagonal elements depends on U_1 and U_4 being non-zero, which can only be true if the spin states of the electrons are mixtures of α and β .

As to the distinctness of the $H^{\xi 1}$ and $H^{\xi 2}$ equations (i.e., whether ξ_1 will be different from ξ_2) comparison of the respective matrices shows clearly that corresponding matrix elements will only be different (except in sign, possibly) from one equation to the other if D_A^1 is different from D_A^2 , or D_B^1 is different from D_B^2 , etc. In other words the spin function can only be different if the electron density on at least one nucleus is different

for the two corresponding orbital functions.

Inspection of the H^{η_1} and H^{η_2} matrices allows a similar comment to be made regarding the distinctness of η_1 and η_2 . These spin functions can only be different if the electron density associated with the two nuclei is different.

In systems where the electron density on the nuclei is the same, the result will simply be that the matrix equations are identical. This implies that there will be no hyperfine structure; a classic example of this is H_2 .

IX-3 Sample Calculation

Considerable reference³¹ has been made to the apparent relation between the coupling constants for a pair of nuclei and the difference in electronegativity of the two nuclei. The perturbation technique has not lent itself to elucidating the relationship. It is possible, albeit in a rather artificial system, to demonstrate this relationship within the context of the approach introduced in section IX-1.

The D_{A1} , D_{B1} , etc., which are constants of the problem, represent the electron density at the nuclei and, as such, are a measure of the electronegativity of the atoms. One then may take the quantity $(D_{A1} + D_{A2}) - (D_{B1} + D_{B2}) = \Delta TD_{AB}$ as a measure of the electronegativity difference between centers A and B. The "coupling" constant of the Ramsey formulation is directly related to the hyperfine

splittings of NMR. Hence the relation of the ΔTD_{AB} to the hyperfine splitting is equivalent to the relation of the electronegativity difference to the coupling constant.

The SCF solution of the four matrix equations gives a common minimum total energy E_g . Since the basis set is two dimensional a second, or excited state, energy and function may be obtained from each of these equations. It should be emphasized that each of these excited energies and functions represents an excited state of the system in which the other three spin-functions retain their ground-state values. One then has the energy level diagram of figure 7. Several arbitrary sets of values for electron densities on the centers A and B were inserted into the equations given in section IX-1 and the SCF energies and functions were obtained from the four matrix equations.

The constants employed and the energies and linear coefficients obtained are displayed in Tables XV and XVI. Figure 8 depicts the relation between these electron density differences at the nuclei and the calculated hyperfine splittings.

The linear relation between ΔTD_{AB} and the hyperfine splitting is certainly parallel to that observed between electronegativity difference and the coupling constant. The ease with which this relationship has been demonstrated may serve to illustrate that various other questions concerning magnetic resonance phenomena may be readily answered when the approach developed here is employed.

Table XV

Data* for illustrating the relation between ΔTD_{AB} and hyperfine splitting.

D_B^1	D_B^2	D_A^1	D_A^2	$D_B^1 + D_B^2$ $= TD_B$	$D_A^1 + D_A^2$ $= TD_A$	$TD_A - TD_B$ $= \Delta TD_{AB}$	Splitting $= \Delta E^?$
0.3	0.3	0.5	0.5	0.6	1.0	0.4	0.8
0.3	0.3	0.6	0.6	0.6	1.2	0.6	1.2
0.3	0.3	0.7	0.7	0.6	1.4	0.8	1.6
0.1	0.1	0.3	0.3	0.2	0.6	0.4	0.8
0.1	0.1	0.4	0.4	0.2	0.8	0.6	1.2
0.1	0.1	0.5	0.5	0.2	1.0	0.8	1.6

* $S_{12} = 0$ in all cases. Only the relative magnitude of the numbers quoted above is significant since no unit is defined.

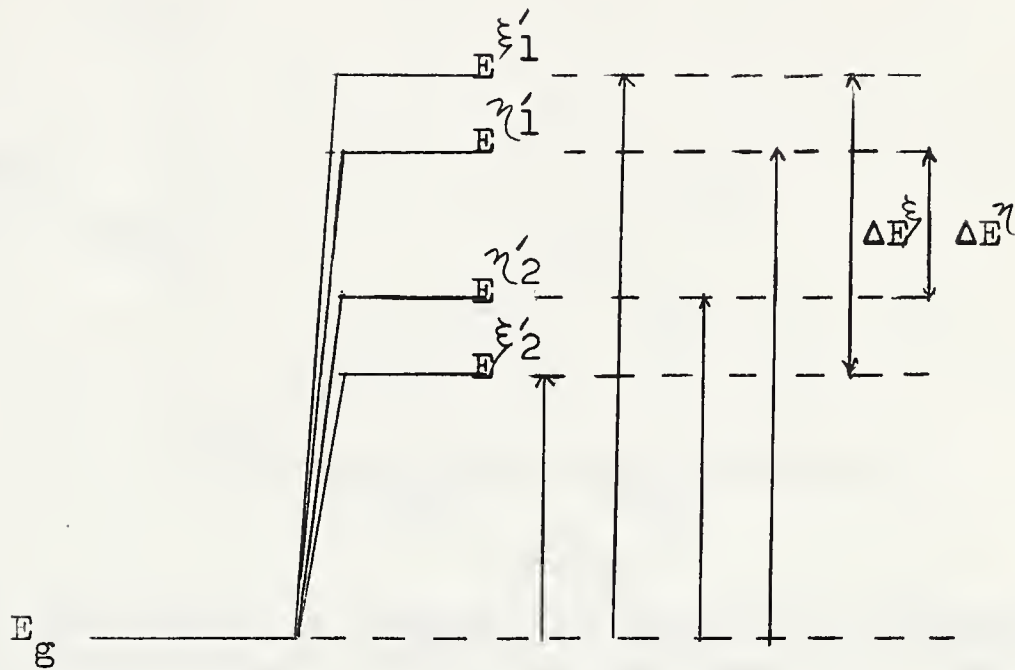
Table XVI

Typical spin function* parameters.

Function	Parameter		Constants
	1	2	
ξ_1	0.027	-0.999	$\left[\begin{array}{l} D_A^1 = 0.3 \\ D_A^2 = 0.3 \\ D_B^1 = 0.5 \\ D_B^2 = 0.5 \\ S_{12} = 0.0 \end{array} \right]$
ξ_1'	0.999	0.027	
ξ_2	0.027	-0.999	
ξ_2'	0.999	0.027	
η_1	0.999	0.027	
η_1'	0.027	-0.999	
η_2	0.999	0.027	
η_2'	0.027	-0.999	

* The unprimed functions refer to the ground state and the primed to the excited state.

Figure 7



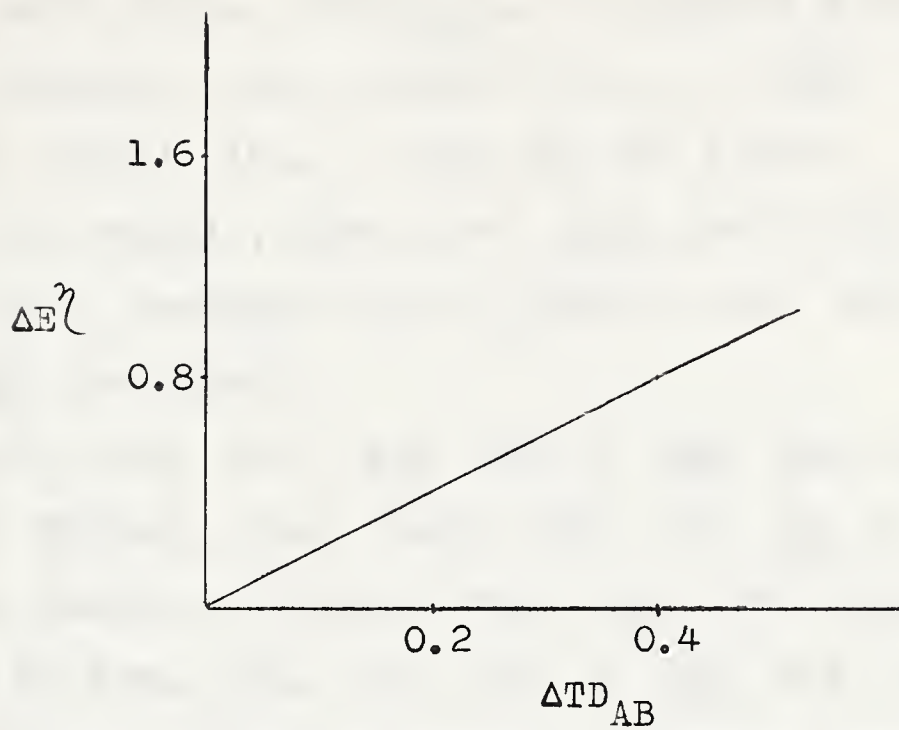
Energy level diagram

Legend:

E_g = minimum or ground state total energy.

The $E_{\xi'_1}$, etc., are the total energy of the system when the function of the matrix designated by ξ_1 has its excited form.

Figure 8



The relation between the hyperfine splitting and the difference in the electron density on two centers.

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APPENDIX I

EVALUATION OF THE GAUSSIAN INTEGRALS

AI-1 The Density Kernel

To find the density kernel for any electron it is first necessary to proceed through some extremely cumbersome notation and untidy equations for one center with many electrons. Hence, the method will be indicated by finding the density kernel for electron one when there are two electrons on one center. Although, as noted, the notation and form of equations can not readily be extended to many electrons, the procedure and sequence of steps which would need to be carried out should be evident.

The density kernel for electron one for the system of two electrons on one center is given as:

$$\begin{aligned}
 I_2 &= \langle \phi_1 / R(\vec{r}', \vec{r}''_1) / \phi_2 \rangle = \int \exp[-m_1 r'^2 - m_j r_2^2 - n_s |\vec{r}' - \vec{r}_2|^2] \\
 &\quad \exp[-m_1 r''^2 - m_j r_2^2 - n_s |\vec{r}'' - \vec{r}_2|^2] d\vec{r}_2 \\
 &= \int \exp[-r'^2(m_1 + n_s) - r''^2(m_1 + n_s)] \\
 &\quad \exp[-r_2^2(m_j + m_j + n_s + n_s) + 2\vec{r}_2(n_s \vec{r}' + n_s \vec{r}'')] d\vec{r}_2
 \end{aligned}$$

The integral part may be written:

$$I_2 = \int \exp[-\Sigma_t g_t r_2^2 + 2\vec{r}_2 \cdot \vec{d}_t] d\vec{r}_2 \quad \text{where}$$

$$g_1 = m_j + n_s \quad ; \quad g_2 = m_j + n_s,$$

$$d_1 = n_s \vec{r}' \quad ; \quad d_2 = n_s \vec{r}''$$

$$I_2 = \int \exp[-\Sigma_t g_t (r_2^2 - 2\vec{r}_2 \frac{\vec{d}_t}{g_t} + \frac{d_t^2}{g_t}) - \frac{d_t^2}{g_t}] d\vec{r}_2$$

$$= \exp\left[\Sigma_t \frac{d_t^2}{g_t}\right] \int \exp\left[-\Sigma_t g_t \left(r_2^2 - 2\vec{r}_2 \cdot \frac{\vec{d}_t}{g_t} + \frac{d_t^2}{g_t}\right)\right] d\vec{r}_2$$

$$I_2 = \exp\left[\Sigma \frac{d_t^2}{g_t}\right] \int \exp\left[-\Sigma_t g_t (\vec{r}_2 - \vec{Q}_t)^2\right] d\vec{r}_2 \quad \text{where } \vec{Q}_t = \frac{d_t}{g_t}$$

This integral can be evaluated as follows:

$I_1 = \int d\vec{r}_m \exp[-\Sigma_s q_s (\vec{r}_m - \vec{Q}_s)^2]$ where $\vec{Q}$ is either some variable not dependent on $\vec{r}_m$ or is a constant.

$$\begin{aligned} I_1 &= \int d\vec{r}_m \exp\left[-\Sigma_s q_s (r_m^2 + Q_s^2 - 2\vec{r}_m \cdot \vec{Q}_s)\right] \\ &= \int d\vec{r}_m \exp\left[-\Sigma_s q_s r_m^2 - 2\Sigma_s q_s \left(\frac{\Sigma_t q_t}{\Sigma_u q_u}\right) \vec{r}_m \cdot \vec{Q}_s + \Sigma_s q_s \left(\frac{\Sigma_t q_t}{\Sigma_u q_u}\right)^2 \right. \\ &\quad \left. - \Sigma q_s \left(\frac{\Sigma_t q_t \vec{Q}_t}{\Sigma_u q_u}\right)^2 + \Sigma_s q_s Q_s^2\right] \\ &= \int d\vec{r}_m \exp\left[-\Sigma_s q_s r_m^2 - 2\Sigma_s q_s \frac{\Sigma_t q_t}{\Sigma_u q_u} \vec{r}_m \cdot \vec{Q}_t \right. \\ &\quad \left. + \Sigma q_s \left(\frac{\Sigma_s q_s \vec{Q}_t}{\Sigma_u q_u}\right)^2 - \Sigma_s q_s \left(\frac{\Sigma_t q_t \vec{Q}_t}{\Sigma_u q_u}\right)^2 + \Sigma_s q_s Q_s^2\right] \\ &= \int d\vec{r}_m \exp\left[-\Sigma_s q_s (r_m^2 - 2\left(\frac{\Sigma_t q_t \vec{Q}_t}{\Sigma_u q_u}\right) \cdot \vec{r}_m + \left(\frac{\Sigma_t q_t \vec{Q}_t}{\Sigma_u q_u}\right)^2)\right] \\ &\quad \exp\left[\frac{\Sigma_s q_s (\Sigma_t q_t \vec{Q}_t)^2}{\Sigma_u q_u \Sigma_u q_u} - \Sigma_s q_s \vec{Q}_s^2\right] \\ &= \int d\vec{r}_m \exp\left[-\Sigma_s q_s \left(\vec{r}_m - \frac{\Sigma q_t \vec{Q}_t}{\Sigma q_u}\right)^2 - \Sigma_s q_s Q_s^2 + \left(\frac{\Sigma q_t \vec{Q}_t}{\Sigma q_u}\right)^2\right] \\ &= \exp\left[-\Sigma_s q_s Q_s^2 + \left(\frac{\Sigma q_t \vec{Q}_t}{\Sigma q_u}\right)^2\right] \int d\vec{r}_m \exp\left[-\Sigma_s q_s \left(\vec{r}_m - \frac{\Sigma_t q_t \vec{Q}_t}{\Sigma_u q_u}\right)^2\right] \end{aligned}$$

By this sequence of steps the integral has become one of

the form $\int d\vec{r}_m \exp[-(r_m - K)^2 \Sigma_s q_s]$ since the portion within the bracket no longer depends on $\underline{s}$, i.e. $\vec{K}$ is a "constant"

$$K = \frac{\Sigma_t q_t \vec{Q}_t}{\Sigma_u q_u} ; \text{ so that, } \int d\vec{r}_m \exp[-b(\vec{r}_m - \vec{K})^2], \text{ where } b = \Sigma_s q_s .$$

For this integral it is noted that as the vector $\vec{r}$ sweeps out its volume element the vector $\vec{r} - \vec{K}$ also sweeps out its volume element. Hence the integrals may be equated as

$$\int d\vec{r}_{mk} \exp[-b r_{mk}^2] = \int d\vec{r}_m \exp[-b r_m^2]$$

which has the value $(\frac{\pi}{b})^{3/2} = (\frac{\pi}{\Sigma q_s})^{3/2}$. This in turn

means that the total integral I_1 is equal to

$$I_1 = \exp[-\Sigma_s q_s Q_s^2 + (\frac{\Sigma_t q_t \vec{Q}_t}{\Sigma_u q_u})^2] (\frac{\pi}{\Sigma q_s})^{3/2}$$

This can be written in a slightly different form if it is noted that

$$(\Sigma_t q_t \vec{Q}_t)^2 = (\Sigma_t q_t \vec{Q}_t)(\Sigma_t q_t \vec{Q}_t) = (\Sigma_s q_s \vec{Q}_s)(\Sigma_t q_t \vec{Q}_t) = \Sigma_s \Sigma_t q_s q_t \vec{Q}_s \cdot \vec{Q}_t$$

and

$$\Sigma q_s Q_s^2 = \frac{\Sigma_u q_u}{\Sigma_u q_u} \Sigma_s q_s Q_s^2 = \frac{\Sigma_t q_t}{\Sigma_u q_u} \Sigma q_s Q_s^2$$

$$= \frac{1/2}{\Sigma_u q_u} (\Sigma_s \Sigma_t q_s q_t Q_s^2 + \Sigma_s \Sigma_t q_s q_t Q_t^2) = \frac{1/2}{\Sigma_u q_u} \Sigma_s \Sigma_t q_s q_t (Q_s^2 + Q_t^2)$$

So that the integral I_1 may be written

$$I_1 = (\frac{\pi}{\Sigma q_s})^{3/2} \exp[\frac{1}{\Sigma_u q_u} - \frac{1}{2} \Sigma_s \Sigma_t q_s q_t (Q_s^2 + Q_t^2) + \Sigma_s \Sigma_t q_s q_t \vec{Q}_s \cdot \vec{Q}_t]$$

$$= (\frac{\pi}{\Sigma q_s})^{3/2} \exp[-\frac{1/2}{\Sigma_u q_u} \Sigma_s \Sigma_t q_s q_t (Q_s^2 + Q_t^2 - 2\vec{Q}_s \cdot \vec{Q}_t)]$$

$$= \left(\frac{\pi}{\Sigma_s q_s} \right)^{3/2} \exp \left[- \frac{1/2}{\Sigma_u q_u} \Sigma_s \Sigma_t q_s q_t (\vec{Q}_s - \vec{Q}_t)^2 \right]$$

$$= \left(\frac{\pi}{\Sigma_s q_s} \right)^{3/2} \exp \left[- \Sigma_t \frac{q_s q_t (\vec{Q}_s - \vec{Q}_t)^2}{\Sigma_u q_u} \right]$$

Finally one then has

$$\int d\vec{r}_m \exp[-\Sigma_s q_s (\vec{r}_m - \vec{Q}_s)^2] = \left(\frac{\pi}{\Sigma_s q_s} \right)^{3/2} \exp \left[- \Sigma_t q_s q_t (\vec{Q}_s - \vec{Q}_t)^2 / \Sigma_u q_u \right].$$

Substitution of this form of the integral into the last equation for I_2 gives

$$\begin{aligned} I_2 &= \exp \left[\Sigma \left(\frac{d_t^2}{g_t} \right) \right] \left(\frac{\pi}{\Sigma_t g_t} \right)^{3/2} \exp \left[- \Sigma_t q_s q_t (\vec{Q}_t - \vec{Q}_s)^2 / \Sigma_t q_t \right] \\ &= \frac{\pi^{3/2} \exp \left[(n_s r')^2 (m_j + n_s)^{-1} + (n_s r'')^2 (m_{j'} + n_{s'})^{-1} \right]}{(m_j + m_{j'} + n_s + n_{s'})^{3/2}} \\ &\quad \exp \left[- \frac{(m_j + n_s)(m_{j'} + n_{s'}) \left[\frac{n_s \vec{r}'}{m_j + n_s} - \frac{n_{s'} \vec{r}''}{m_{j'} + n_{s'}} \right]^2}{(m_j + m_{j'} + n_s + n_{s'})} \right] \end{aligned}$$

And the total density kernel for electron one is:

$$\begin{aligned} I_2 &= \frac{\pi^{3/2}}{(m_j + m_{j'} + n_s + n_{s'})^{3/2}} \exp \left[-r'^2 (m_i + n_s) - r''^2 (m_{i'} + n_{s'}) \right. \\ &\quad \left. + \frac{(n_s r')^2}{m_j + n_s} + \frac{(n_{s'} r'')^2}{m_{j'} + n_{s'}} - \frac{(m_j + n_s)(m_{j'} + n_{s'}) \left[\frac{n_s \vec{r}'}{m_j + n_s} - \frac{n_{s'} \vec{r}''}{m_{j'} + n_{s'}} \right]^2}{m_j + m_{j'} + n_s + n_{s'}} \right] \\ &= \left(\frac{\pi}{m_j + m_{j'} + n_s + n_{s'}} \right)^{3/2} \exp \left[-r'^2 \left(m_i + \frac{n_j n_s}{m_j + n_s} \right) \right. \\ &\quad \left. - r''^2 \left(m_{i'} + \frac{m_{j'} n_{s'}}{m_{j'} + n_{s'}} \right) - \frac{(m_j + n_s)(m_{j'} + n_{s'})}{(m_j + m_{j'} + n_s + n_{s'})} \left[\frac{n_s \vec{r}'}{m_j + n_s} - \frac{n_{s'} \vec{r}''}{m_{j'} + n_{s'}} \right]^2 \right] \end{aligned}$$

It is advantageous to have the density kernel in the form

$$I_2 = G_1 \exp[-a r'^2 - b r''^2 + c(\vec{r}' - \vec{r}'')^2]$$

The required values of $\underline{a}$, $\underline{b}$, $\underline{c}$ and $\underline{G}$ may be obtained by expanding the square in this last equation and the square in the one previous to it, collecting the coefficients of r'^2 , r''^2 and $\vec{r}' \cdot \vec{r}''$, equating the appropriate coefficients and solving the simultaneous equations to give

$$a_1 = m_i + n_s - \frac{n_s(n_s + n_{s'})}{(m_j + m_{j'} + n_s + n_{s'})}$$

$$b_1 = m_{i'} + n_{s'} - \frac{n_{s'}(n_{s'} + n_s)}{(m_j + m_{j'} + n_s + n_{s'})}$$

$$c_1 = \frac{n_s n_{s'}}{(m_j + m_{j'} + n_s + n_{s'})}$$

$$G_1 = (m_j + m_{j'} + n_s + n_{s'})^{-3/2} \pi^{3/2}$$

It should be emphasized that although other rather obvious approaches to the solution of the integral may be used in this simple problem the particular approach indicated is the most satisfactory in the more complex case of many electrons and many centers.

AI-2 The Potential Energy Integral for Electron One

$$I_3 = \langle \phi_1 / 1/r_1 / \phi_2 \rangle$$

And from the definition of the density kernel this becomes

$$I_3 = \int d\vec{r} P(\vec{r}/\vec{r}') P(\vec{r}/\vec{r}'') \left[\frac{1}{r} \right] \langle \phi_1 / R(\vec{r}', \vec{r}'', 1) / \phi_2 \rangle .$$

For the above form of the density kernel this becomes

$$\begin{aligned} I_3 &= G_1 \int d\vec{r} P(\vec{r}/\vec{r}') P(\vec{r}/\vec{r}'') \left[\frac{1}{r} \right] \exp[-a_1 \vec{r}'^2 - b_1 \vec{r}''^2 - c(\vec{r}' - \vec{r}'')^2] \\ &= G_1 \int d\vec{r} \frac{1}{r} \exp[-r^2(a_1 + b_1)] = 2\pi \frac{G_1}{(a_1 + b_1)} \end{aligned}$$

AI-3 The Kinetic Energy Integral

The kinetic energy integral for electron one is

$I_4 = \langle \phi_1 / -\frac{1}{2} \Sigma_i^3 \left(\frac{\partial}{\partial r_i} \right)^2 / \phi_2 \rangle$ where $\Sigma_i^3 \left(\frac{\partial}{\partial r_i} \right)^2$ is the Laplacian operator in cartesian coordinates r_x, r_y, r_z , and in terms of the density kernel, I_4 becomes

$$\begin{aligned} I_4 &= \frac{G_1}{2} \Sigma_{xyz}^3 \int d\vec{r} P(\vec{r}/\vec{r}') P(\vec{r}/\vec{r}'') \left(\frac{\partial}{\partial r_x''} \right)^2 \\ &\quad \exp[-a_1 r'^2 - b_1 r''^2 - c_1 (\vec{r}' - \vec{r}'')^2] \\ &= \frac{G_1}{2} \Sigma_{xyz}^3 \int d\vec{r} P(\vec{r}/\vec{r}') P(\vec{r}/\vec{r}'') \left(\frac{\partial}{\partial r_x''} \right) (-2b r_x'' - 2c r_x'' + 2c r_x') \\ &\quad \exp[-a r'^2 - b r''^2 - c r'^2 + r''^2 - 2(r_x' r_x'' + r_y' r_y'' + r_z' r_z'')]] \\ &= G \Sigma_{xyz} \int d\vec{r} P(\vec{r}/\vec{r}') P(\vec{r}/\vec{r}'') \\ &\quad \exp[-a r'^2 - b r''^2 - c (\vec{r}' - \vec{r}'')^2] \{ b + c - 2 (b r_x'' + c r_x'' - c r_x')^2 \} \end{aligned}$$

Operation of the replacement operators may now be carried out to give

$$\begin{aligned} I_4 &= G_1 \Sigma_i \int d\vec{r} \exp[-r^2(a+b)] \{ b_1 + c_1 - 2b_1^2 (r_x)^2 \} \\ &= G_1 \int d\vec{r} (3b_1 + 3c_1 - 2b_1^2 r^2) \exp[-r^2(a_1 + b_1)]] \\ &= G_1 [3b_1 + 3c_1 + 2b_1^2 \frac{\partial}{\partial b}] \int d\vec{r} \exp[-r^2(a_1 + b_1)]] \\ &= G_1 [3b_1 + 3c_1 + 2b_1^2 \frac{\partial}{\partial b}] \left(\frac{\pi}{a_1 + b_1} \right)^{3/2} \\ &= G_1 \left(\frac{\pi}{a_1 + b_1} \right)^{3/2} (3b_1 + 3c_1) - 3b^2 \frac{\pi^3}{(a_1 + b_1)^{5/2}} \\ &= \frac{G_1^{3/2}}{(a_1 + b_1)^{5/2}} 3(a_1 b_1 + b_1 c_1 + a_1 c_1) \end{aligned}$$

AI-4 Electronic Repulsion Integral

The repulsion integral for electrons one and two on the same center has the form:

$$\begin{aligned}
 I_5 &= \langle \exp[-m_i r_i^2 - m_j r_2^2 - n_s r_{12}^2] \mid \frac{1}{r_{12}} \mid \\
 &\quad \exp[-m_i r_1^2 - m_j r_2^2 - n_s r_{12}^2] \rangle \\
 &= \int d\vec{r}_1 \exp[-U r_1^2] \int d\vec{r}_2 \frac{1}{r_{12}} \exp[-V r_2^2 - W r_{12}^2] \\
 &\quad \text{where } U = m_i + m_i, \\
 &\quad \quad V = m_j + m_j, \\
 &\quad \quad W = n_s + n_s,
 \end{aligned}$$

The inner integral is defined as

$$I_{5i} = \int d\vec{r}_2 \frac{1}{r_{12}} \exp[-V r_2^2 - W r_{12}^2]$$

and it is noted that for this integration electron one is fixed.

From the law of cosines one has

$$r_2^2 = r_{12}^2 + r_1^2 - 2r_{12}r_1 \cos \varnothing, \text{ where } \varnothing \text{ is the angle between } r_2 \text{ and } r_{12}.$$

It is also seen (as for I_1) that as $\vec{r}_2$ sweeps out its volume elements that $\vec{r}_{12}$ also moves through its volume element.

$$\begin{aligned}
 I_{5i} &= \int \frac{\exp[-V r_2^2 - W r_{12}^2] d\vec{r}_2}{r_{12}} = \int \frac{d\vec{r}_{12} \exp[-V r_2^2 - W r_{12}^2]}{r_{12}} \\
 &= \int_{r_{12}}^{r_{12}^2} \sin \theta d\theta d\varnothing dr_{12} \exp[-V r_2^2 - W r_{12}^2]
 \end{aligned}$$

$$= 2\pi \int r_{12} \sin \theta \, d\theta \, dr_{12} \exp[-Vr_2^2 - Wr_{12}^2]$$

On using the cosine law form for r_2^2 this becomes

$$I_{5i} = 2\pi \int \exp[-Vr_1^2] \exp[-r_{12}^2 (V+W) + V(2r_{12}r_1) \cos \theta] \\ r_{12} dr_{12} \sin \theta \, d\theta$$

Integrating over θ gives

$$I_{5i} = \frac{\exp[-Vr_1^2]}{Vr_1} \left\{ \int \frac{r_{12}}{r_{12}} dr_{12} \exp[-(V+W)r_{12}^2 + 2Vr_1r_{12}] - \int dr_{12} \frac{r_{12}}{r_{12}} \right. \\ \left. \exp[-(V+W)r_{12}^2 - 2Vr_1r_{12}] \right\}$$

On completing the squares in each exponent in the integral this becomes

$$I_{5i} = \frac{\exp[-Vr_1^2]}{Vr_1} \left\{ \exp\left[\frac{Vr_1}{V+W}\right] \int dr_{12} \exp[-(V+W)\left(r_{12} - \frac{V}{V+W}r_1\right)^2] \right. \\ \left. - \exp\left[\frac{Vr_1^2}{V+W}\right] \int dr_{12} \exp[(V+W)\left(r_{12} + \frac{V}{V+W}r_1\right)^2] \right\} \\ = \frac{\exp\left[-\frac{VWr_1^2}{V+W}\right]}{Vr_1} \left\{ \int_{-a}^{\infty} \exp[-(V+W)y^2] dy - \int_a^{\infty} \exp[-(V+W)y'^2] dy' \right\}$$

$$\text{with } y = r_{12} - \frac{Vr_1}{V+W} ; y' = \left(r_{12} - \frac{Vr_1}{V+W}\right) ; a = \frac{Vr_1}{V+W}$$

$$I_{5i} = \frac{\pi \exp\left[-\frac{VWr_1^2}{V+W}\right]}{Vr_1} \left[\int_0^{\infty} \exp[-(V+W)y^2] dy + \int_{-a}^{\infty} \exp[-(V+W)y^2] dy \right. \\ \left. - \int_0^{\infty} \exp[-(V+W)y'^2] dy' - \int_a^{\infty} \exp[-(V+W)y'^2] dy' \right]$$

$$\text{The integral } \int_0^{\infty} \exp[-(V+W)y^2] dy \equiv \int_0^{\infty} \exp[-(V+W)y'^2] dy'$$

since the y is really a dummy variable so that the value of the integral depends only on the limits. Hence the last line can be written as

$$I_{5i} = \frac{\pi \exp\left[-\frac{VWr_1^2}{V+W}\right]}{Vr_{11}} \left\{ \int_0^a \exp[-(V+W)y'^2] dy' + \int_{-a}^0 \exp[-(V+W)y^2] dy \right\}.$$

$y' = r_{12} + a$ and for the allowed range of the first integral $0 \leq y' \leq a$; therefore $0 \leq r_{12} + a \leq a$ and hence $-a \leq r_{12} \leq 0$. $y = r_{12} - a$ and for the allowed value of the second integral $-a \leq y \leq 0$, therefore $-a \leq r_{12} - a \leq 0$ and hence $0 \leq r_{12} \leq a$.

Thus in the two integrals r_{12} has the range $-a \leq r_{12} \leq a$ (i.e., the ranges of y and y' have the same range for r_{12}).

The two integrals can be combined in terms of the variable r_{12} as

$$I_{5i} = \frac{\pi \exp\left[-\frac{VWr_1^2}{V+W}\right]}{Vr_1} \int_{-a}^a \exp[-(V+W)r_{12}^2] dr_{12}$$

which, since $\exp[-(V+W)r_{12}^2]$ is an even function, gives

$$I_{5i} = \frac{2\pi}{Vr_1} \exp\left[-\frac{VWr_1^2}{V+W}\right] \int_0^a \exp[-(V+W)r_{12}^2] dr_{12}$$

With the substitution of $r_{12} = \frac{V}{V+W} z$, the integral becomes

$$= \frac{2\pi}{r_1(V+W)} \exp\left[-\frac{VW}{V+W} r_1^2\right] \int_0^{r_1} \exp\left[-\frac{V^2}{V+W} z^2\right] dz$$

The total integral on substitution for I_{5i} becomes

$$I_5 = \int d\vec{r}_1 \exp[-Ur_1^2] \frac{2\pi}{r_1(V+W)} \exp\left[-\frac{VW}{V+W} r_1^2\right] \int_0^{r_1} \exp\left[-\frac{V^2}{V+W} z^2\right] dz$$

$$= \frac{2\pi}{V+W} \int d\vec{r}_1 \frac{1}{r_1} \exp[-Ur_1^2 - \frac{VW}{V+W} r_1^2] \int_0^{r_1} \exp[-\frac{Vz^2}{V+W}] dz$$

$$= \frac{2}{V+W} \int d\vec{r}_1 \frac{1}{r_1} \exp[-Gr_1^2] \int_0^{r_1} \exp[-Hz^2] dz \text{ with}$$

$$(UV + UW + VW)(V+W) = G \text{ and } H = \frac{V^2}{V+W}$$

$$I_5 = \frac{2\pi}{V+W} \frac{V^2(V+W)}{V^2(V+W)} \int d\vec{r}_1 \frac{1}{r_1} \exp[-Gr_1^2] \int_0^{r_1} \exp[-Hz^2] dz$$

$$= \left(\frac{V}{V+W}\right)^2 \frac{2\pi}{\frac{V^2}{(V+W)}} \int d\vec{r}_1 \frac{1}{r_1} \exp[-Gr_1^2] \int_0^{r_1} \exp[-Hz^2] dz$$

$$= \left(\frac{V}{V+W}\right)^2 \left[-\frac{2\pi}{H} \int d\vec{r}_1 \frac{1}{r_1} \exp[-Gr_1^2] \int_0^{r_1} \exp[-Hz^2] dz \right]$$

The integral $\int d\vec{r}_1 \frac{1}{r_1} \exp[-Gr_1^2] \int_0^{r_1} \exp[-Hz^2] dz$ is readily found by standard methods¹² to give

$$I_5 = \left(\frac{V}{V+W}\right)^2 \frac{2(\pi)^{5/2}}{GH(G+H)^{1/2}} = \frac{2(\pi)^{5/2}(U+V)^{-1/2}}{(UV + WV + UW)} \text{ which is taken}$$

as the form of the electron repulsion integral.

AI-5 Overlap Integral

The overlap integral I_6 is given for two electrons and the method is readily extended to more than two electrons

$$I_6 = \langle \phi_1 / \phi_2 \rangle = \left(\prod_i \int d\vec{r}_i \right) \exp[-m_i r_1^2 - m_j r_2^2 - n_s r_{12}^2]$$

$$\exp[-m_i r_1^2 - m_j r_2^2 - n_s r_{12}^2]$$

$$= \left(\prod_i^2 \int d\vec{r}_i \right) \exp[-\sum_i r_i^2 a_i - \sum_{ij} c_{ij} r_{ij}^2]$$

where

$$a_1 = (m_i + m_{i'}) \quad ; \quad a_2 = (m_j + m_{j'})$$

$$c_{12} = \frac{(n_s + n_{s'})}{2} \quad ; \quad c_{21} = \frac{(n_s + n_{s'})}{2}$$

$$\begin{aligned} I_6 &= \left(\prod_i^2 \int d\vec{r}_i \right) \exp[-\sum_i r_i^2 (a_i + 2\sum_{ij} c_{ij}) + 2\sum_{ij} (r_i r_j) c_{ij}] \\ &= \left(\prod_i^2 \int d\vec{r}_i \right) \exp[-\sum_{ij} r_i r_j d_{ij}] \end{aligned}$$

where

$$d_{ii} = a_i + \sum_{ij} c_{ij} \quad ; \quad d_{ij} = -2c_{ij}$$

$$I_6 = \pi_{xyz} \left(\prod_i \int dx_i \right) \exp[-\sum_{ij} x_i d_{ij} x_j]$$

To perform the integration of the last line it is first necessary to show that

$$\left(\prod_i \int dx_i \right) \exp[-\sum_{ij} x_i d_{ij} x_j] = \left(\prod_i \int dy_i \right) \exp[-\sum_i y_i^2 c_i] = \frac{\pi^{1/2}}{\prod_i c_i}$$

This can be seen as follows: the integral may first be written in terms of the matrix $\underline{D}$ and the vectors $\underline{x}$ (whose components are x_i , etc.) as

$$\left(\prod_i \int dx_i \right) \exp[-\sum_{ij} x_i d_{ij} x_j] = \left(\prod_i \int dx_i \right) \exp[-\vec{x}^+ \underline{D} \vec{x}] ,$$

Putting $\vec{x} = \underline{Q} \vec{y}$; $\vec{x}^+ = \vec{y}^+ \underline{Q}^+$, and therefore, $\vec{x}^+ \underline{D} \vec{x} = \vec{y}^+ \underline{Q}^+ \underline{D} \underline{Q} \vec{y} = \vec{y}^+ \underline{B} \vec{y}$, with $\underline{B} = \underline{Q}^+ \underline{D} \underline{Q}$.

Clearly if $\underline{B}$ were diagonal then $\vec{y}^+ \underline{B} \vec{y}$ would be a sum of squares and hence the desired form. The problem then is to obtain the $\underline{Q}$ which will diagonalize the matrix $\underline{B}$. $\underline{Q}$ can be obtained by a standard method¹³.

For the case of $n=2$

$$\underline{D} = \begin{pmatrix} D_{11} & D_{12} \\ D_{21} & D_{22} \end{pmatrix} \text{ so that } \underline{Q} = \begin{pmatrix} 1 & -D_{12}/D_{11} \\ 0 & 1 \end{pmatrix} \text{ and } \underline{Q}^+ \underline{D} \underline{Q} = \begin{pmatrix} D_{11} & 0 \\ 0 & \frac{|D|}{D_{11}} \end{pmatrix}$$

$$\text{therefore } \bar{x}^+ \underline{D} \bar{x} = \bar{y}^+ \underline{Q}^+ \underline{D} \underline{Q} \bar{y} = \bar{y}^+ \begin{pmatrix} D_{11} & 0 \\ 0 & \frac{|D|}{D_{11}} \end{pmatrix} \bar{y}$$

$$= \sum_i B_{ii} y_i^2 \text{ where } B_{11} = D_{11}, B_{22} = \frac{|D|}{D_{11}}$$

Hence

$$\begin{aligned} (\prod_i \int dx_i) \exp[-\sum_{ij} x_i d_{ij} x_j] &= (\prod_i \int dy_i) \exp[-\sum_i B_{ii} y_i^2] \\ &= \frac{\pi^{1/2}}{(\prod_i B_{ii})^{1/2}} = \frac{\pi^{1/2}}{|D|^{1/2}} \text{ since} \end{aligned}$$

$$\prod_i B_{ii} = (D_{11}) (D_{22} - D_{12}^2/D_{11}) = D_{11} D_{22} - D_{12}^2 = |D|.$$

Then the integral

$$\begin{aligned} I_6 &= \prod_{xyz} \left(\prod_i \int dx_i \right) \exp[-\sum_{ij} x_i d_{ij} x_j] \\ &= \prod_{xyz} \left(\frac{\pi^{1/2}}{|D|^{1/2}} \right)^n = \frac{\pi^{3/2}}{(|D|)^{3/2}} \text{ for } n = 3 \end{aligned}$$

Evaluating this for two electrons one has

$$I_6 = \left[\frac{\pi}{D_{11} D_{22} - D_{12}^2} \right]^{3/2} = \frac{\pi}{(m_i + m_i', + n_s + n_{s'}) (m_j + m_j', + n_s + n_{s'}) - (n_s + n_{s'})^2}^{3/2}$$

$$I_6 = \left(\frac{\pi}{UV + (U+V)W} \right)^{3/2}$$

Which is the final form of the overlap integral.

In Boys' paper he requires that $\underline{D}$ be a positive definite matrix in order that a real number be obtained by the square

root operation. This is true if the parameters forming U, V, W are all positive (see denominator in the last line above).

APPENDIX II

SOLUTION OF THE MATRIX EQUATIONS

AII-1 Solution of the Matrix Equations

The solution by the Jacobian technique, of the eigenvalue matrix equation, $\underline{H}\vec{c} = \underline{E}\vec{c}$, where the basis functions are not mutually orthonormal, must be approached by transforming this equation to the equivalent form $\underline{H}'\vec{\lambda} = \underline{E}\vec{\lambda}$ where the basis functions are orthonormal.

The relation of the two equations can be established in the following manner. Defining a matrix $\underline{T}$ by $\underline{T}^+\underline{T} = \underline{S}$ and substituting in $\underline{H}\vec{c} = \underline{E}\vec{c}$ gives : $\underline{H}\vec{c} = \underline{E}\underline{T}^+\underline{T}\vec{c}$. Inserting $\underline{I} = \underline{T}^{-1}\underline{T}$ into the equation leads to $\underline{H}\underline{T}^{-1}\underline{T}\vec{c} = \underline{E}\underline{T}^+\underline{T}\vec{c}$. This form reduces to $(\underline{T}^+)^{-1}\underline{H}\underline{T}^{-1}\underline{T}\vec{c} = \underline{E}\underline{T}\vec{c}$ on left multiplication by $(\underline{T}^+)^{-1}$. Defining $\underline{m} = \underline{T}^{-1}$ allows the equation to be written as

$$\underline{H}'\vec{\lambda} = \underline{E}\vec{\lambda} \quad \text{with } \underline{H}' = \underline{m}^+\underline{H}\underline{m} \text{ and } \vec{\lambda} = \underline{m}^{-1}\vec{c}$$

In asking for the solutions of $\underline{H}'\vec{c} = \underline{E}\vec{c}$ one is asking for the eigenvectors and eigenvalues of the set of equations

$$\begin{aligned} \underline{H}\vec{c}_1 &= \underline{E}_1\underline{S}\vec{c}_1 \\ \underline{H}\vec{c}_2 &= \underline{E}_2\underline{S}\vec{c}_2, \text{etc.} \end{aligned}$$

a set of equations which can be represented by the one matrix equation $\underline{H}\underline{C} = \underline{E}\underline{S}\underline{C}$ where $\underline{C}$ is now a square matrix and $\underline{E}$ a diagonal matrix. The Schmidt Orthonormalization method (SOMS) given in the next section can then be employed to obtain the $\underline{m}$ matrix required to transform this equation to the form $\underline{H}'\vec{\lambda} = \underline{E}\vec{\lambda}$.

The Jacobian Technique described in section AII-3 generates a $\underline{\lambda}$ such that $\underline{\lambda}^+\underline{H}'\underline{\lambda} = \underline{H}''$ is a diagonal matrix with

$$\underline{\lambda}^+ \underline{\lambda} = \underline{I}.$$

Writing out the equation $\underline{\lambda}^+ \underline{H}' \underline{\lambda} = \underline{E} \underline{\lambda}^+ \underline{\lambda}$ element by element gives

$$\vec{\lambda}_1^+ \underline{H}' \vec{\lambda}_1 = E_1$$

$$\vec{\lambda}_2^+ \underline{H}' \vec{\lambda}_2 = E_2$$

so that the vectors $\vec{\lambda}_i$ are eigenvectors of the matrix $\underline{H}'$ with eigenvalues E_i . But these last equations become $\vec{\lambda}_i^+ \underline{m}^+ \underline{H} \underline{m} \vec{\lambda}_i = E_i$ on substituting for $\underline{H}'$. Writing $\vec{c}_i$ as $\underline{m} \vec{\lambda}_i$ the equation becomes

$$\vec{c}_i^+ \underline{H} \vec{c}_i = E_i$$

and the vectors $\vec{c}_i$ are the eigenvectors of the matrix $\underline{H}$ with eigenvalues E_i .

Since it is the lowest eigenvalue that is required a search (EVSS) of the eigenvalues E_i must be carried out. The vector $\vec{c}$ corresponding to the lowest E will be given by $\underline{m} \vec{\lambda}_i$ where $\vec{\lambda}_i$ is the row of the $\underline{\lambda}$ matrix corresponding to the row in $\underline{E}$ in which the lowest E_i occurs.

AII-2 Schmidt Orthonormalization (SOMS)

The orthonormal set of functions φ_i generated by the Schmidt Orthonormalization procedure from a non-orthonormal set φ'_i are related for a set of n functions by

$$\varphi_i = \sum_{j=1}^i m_{ij} \varphi'_j, \quad i = 1 \dots n$$

AII-1

Such a form introduces $\frac{n(n+1)}{2}$ parameters m_{ij} to be determined subject to the $\frac{n(n+1)}{2}$ orthonormality conditions

$$\langle \varphi_i / \varphi_j \rangle = \delta_{ij}.$$

Expanding $\langle \varphi_i / \varphi_j \rangle$ gives

$$\begin{aligned} \langle \varphi_i / \varphi_j \rangle &= \langle \sum_k^i m_{ik} \varphi'_k / \sum_l^j m_{jl} \varphi'_l \rangle \\ &= \sum_k^i \sum_l^j m_{ik} S'_{kl} m_{jl} \text{ where } S'_{ij} = \langle \varphi'_i / \varphi'_j \rangle \end{aligned}$$

Taking $\langle \varphi_i / \varphi_j \rangle = S_{ij}$ as a matrix element one obtains $\underline{S} = \underline{m}^+ \underline{S}' \underline{m}$ and the matrix $\underline{m}$ has the triangular form required by equation AII-1.

In view of this, the matrix operation $\underline{m}^+ \underline{S}' \underline{m}$ to give a unit matrix for the solution of the matrix equations can indeed be taken as simply a transformation to an orthonormal basis set.

The explicit form of the matrix element m_{ij} is most conveniently found by first finding T_{ij} , such that $\underline{T}^+ \underline{T} = \underline{S}$, for simple cases and then obtaining by induction:

$$T_{in} = (S_{in} - \sum_{k < i} T_{ki} T_{kn})^{1/2} / T_{ii}$$

$$T_{nn} = (S_{nn} - \sum_{k < n} T_{kn}^2)^{1/2}$$

Since $\underline{m} = \underline{T}^{-1}$, one can obtain the elements of $\underline{m}$ by the identity $\underline{m} \underline{T} = \underline{I}$; obtaining finally $m_{ii} = 1/T_{ii}$

$$m_{(i < n)} = -\sum_{k < i}^{n-1} m_{ik} T_{kn} / T_{nn}.$$

AII-3 Jacobi Diagonalization of H'

The problem is essentially that of finding the matrix $\underline{\lambda}$ which will reduce the off-diagonal elements to zero or as close to zero as required in $\underline{\lambda}^+ \underline{H}' \underline{\lambda} = \underline{H}''$.

The largest off-diagonal element is determined and the matrix $\underline{\lambda}_1$ found which will reduce the value of this element in $\underline{H}'_1$ to zero with the orthogonal transformation $\underline{\lambda}_1^+ \underline{H}'_1 \underline{\lambda}_1 = \underline{H}'_1$. Although this transformation certainly alters the values of the other elements in $\underline{H}'_1$ it is convergent for the change is primarily towards an increase in weight along the diagonal and in fact it can be shown¹⁴ that for any off-diagonal element $H'_{lrs} < H'_{rs}$. The process is repeated, each time the largest element in the transformed matrix being determined and a new $\underline{\lambda}_m$ found until finally the largest off-diagonal element is effectively zero and the matrix $\underline{\lambda} = \underline{\lambda}_1 \underline{\lambda}_2 \dots \underline{\lambda}_n$ has been found which diagonalizes $\underline{H}'$ as $\underline{\lambda}^+ \underline{H}' \underline{\lambda} = \underline{H}''$.

The formulation of the matrix $\underline{\lambda}_m$ is given explicitly by Greenstadt¹⁴ and a method developed there for solving the trigonometric equations which is stable against singularities and rounding errors of machine calculations.

APPENDIX III

VARIATIONS OF THE BASIS SET

AI-1 Mavle

The logical question of the direction of change for a better value of a particular exponential parameter $\underline{m}$ is established and answered by changing $\underline{m}$ by $\pm \Delta m$ and calculating the energies. Knowing this, change is carried out in the proper direction until the energy begins to rise. At this point the region of the minimum has been established and a value for $\underline{m}$ on either side of the minimum determined.

The value of the increment is then decreased by a factor of two and the proper direction of change again established. As before, alteration of the parameter is continued in the proper direction until the minimum is bracketed - this time more closely than before. The process is continued until the value of $\underline{m}$ for the minimum has been determined to any desired accuracy.

Having established a temporary best value for this parameter a search for a best value of the next parameter is initiated and the value found. The procedure is continued until the temporary best values for all the parameters have been determined. A new cycle is then begun with the variation of the first parameter and the process continued until it is found that the temporary best values remain unchanged for two successive cycles and can be taken as the best values for the exponential parameters.

APPENDIX IV

INTEGRALS FOR THE BASIS FUNCTIONS α AND β

AIV-1 The S Matrices

The general term, $S_{mm'}^{\xi 1}$, for the matrix $\underline{S}^{\xi 1}$ is

$$\begin{aligned} S_{mm'}^{\xi 1} &= \langle \psi_1 \psi_{2\sigma_m} \xi_2 \eta_1 \eta_2 / (\psi_1 \psi_{2\sigma_m} \xi_2 - \psi_2 \psi_1 \xi_{2\sigma_m}) \eta_1 \eta_2 \rangle \\ &= \langle \eta_1 / \eta_1 \rangle \langle \eta_2 / \eta_2 \rangle \langle \psi_1 \psi_{2\sigma_m} \xi_2 / (\psi_1 \psi_{2\sigma_m} \xi_2 - \psi_2 \psi_1 \xi_{2\sigma_m}) \rangle \\ &= \eta_{11} \eta_{22} [\delta_{mm'} \xi_{22} - S_{12}^2 \Sigma_{mm'} g_n g_n \delta_{mn} \delta_{nm'}] \end{aligned}$$

where the electrons always occur in the order 1,2 and

the nuclei as 1,2 and $S_{12} = \langle \psi_1 / \psi_2 \rangle \eta_{pq} = \langle \eta_p / \eta_q \rangle$,

$\xi_{ij} = \langle \xi_i / \xi_j \rangle$, and δ_{ij} is the Kronecker delta. Similarly one obtains

$$S_{nn'}^{\xi 2} = \eta_{11} \eta_{22} [\delta_{nn'} \xi_{11} - S_{12}^2 \Sigma_{mm'} g_m g_m \delta_{mn} \delta_{nm'}]$$

$$S_{rr'}^{\eta 1} = [\xi_{11} \xi_{22} - S_{12}^2 v_1^2] \delta_{rr'} \eta_{22}$$

$$S_{ss'}^2 = [\xi_{11} \xi_{22} - S_{12}^2 v_1^2] \delta_{ss'} \eta_{11}$$

where $v_1 = \xi_{12} = g_1^m g_1^n + g_2^m g_2^n$.

AIV-2 The H Matrices

For $H^{\xi 1}$ matrix the general element is

$$\begin{aligned} H_{mm'}^{\xi 1} &= \langle \psi_1 \psi_{2\sigma_m} \xi_2 \eta_1 \eta_2 / \Sigma_k \Sigma_N \delta_{r_{kN}} \vec{S}_k \cdot \vec{I}_N / \psi_1 \psi_{2\sigma_m} \xi_2 \eta_1 \eta_2 \rangle \\ &\quad - \langle \psi_1 \psi_{2\sigma_m} \xi_2 \eta_1 \eta_2 / \Sigma_k \Sigma_N \delta_{r_{kN}} \vec{S}_k \cdot \vec{I}_N / \psi_2 \psi_1 \xi_{2\sigma_m} \eta_1 \eta_2 \rangle \\ &= H_{mm'}^{\xi 1}(1) - H_{mm'}^{\xi 1}(2) \end{aligned}$$

These two terms will be treated separately and then

recombined. For the first term

$$\begin{aligned}
 H_{mm}^{\xi 1, (1)} &= \langle \psi_1 \psi_2^{\sigma_m} \xi_1 \eta_1 \eta_2 / \vec{S}_1 \cdot (\delta_{1A} \vec{I}_A + \delta_{1B} \vec{I}_B) / \psi_1 \psi_2^{\sigma_m} \xi_2 \eta_1 \eta_2 \rangle \\
 &+ \langle \psi_1 \psi_2^{\sigma_m} \xi_2 \eta_1 \eta_2 / \vec{S}_2 \cdot (\delta_{2A} \vec{I}_A + \delta_{2B} \vec{I}_B) / \psi_1 \psi_2^{\sigma_m} \xi_2 \eta_1 \eta_2 \rangle \\
 &= \xi_{22} \langle \sigma_m / \vec{S}_1 / \sigma_m \rangle [D_A^1 \eta_{22} \langle \eta_1 / \vec{I}_A / \eta_1 \rangle + D_B^1 \eta_{11} \langle \eta_2 / \vec{I}_B / \eta_2 \rangle] \\
 &+ \delta_{mm} \langle \xi_2 / \vec{S}_2 / \xi_2 \rangle \cdot [D_A^2 \eta_{22} \langle \eta_1 / \vec{I}_A / \eta_1 \rangle + D_B^2 \eta_{11} \\
 &\langle \eta_2 / \vec{I}_B / \eta_2 \rangle]
 \end{aligned}$$

where A and B refer to the nuclei and 1 and 2 to the electrons and

$$\begin{aligned}
 D_A^1 &= \langle \psi_1(1) / \delta_{1A} / \psi_1(1) \rangle ; & D_A^2 &= \langle \psi_2(2) / \delta_{2A} / \psi_2(2) \rangle \\
 D_B^1 &= \langle \psi_1(1) / \delta_{1B} / \psi_1(1) \rangle ; & D_B^2 &= \langle \psi_2(2) / \delta_{2B} / \psi_2(2) \rangle
 \end{aligned}$$

The scalar product $\vec{S}_k \cdot \vec{I}_N$ can be written as $\vec{S}_k : \vec{I}_N = S_{kx} I_{Nx} + S_{ky} I_{Ny} + S_{kz} I_{Nz}$ and since the bra-ket notation has put the functions and operators together correctly one can write

$$H_{mm}^{\xi 1, (1)} = H_{mm}^{\xi 1, (1x)} + H_{mm}^{\xi 1, (1y)} + H_{mm}^{\xi 1, (1z)} ; \text{ where, for}$$

example,

$$\begin{aligned}
 H_{mm}^{\xi 1, (1x)} &= \xi_{22} \langle \sigma_m / S_x / \sigma_m \rangle [D_A^1 \langle \eta_1 / I_x / \eta_1 \rangle \eta_{22} \\
 &+ D_B^1 \eta_{11} \langle \eta_2 / I_x / \eta_2 \rangle] + \delta_{mm} \langle \xi_2 / S_x / \xi_2 \rangle [D_A^2 \eta_{22} \langle \eta_1 / I_x / \eta_1 \rangle \\
 &+ D_B^2 \eta_{11} \langle \eta_2 / I_x / \eta_2 \rangle]
 \end{aligned}$$

From the relations, $S_x \alpha = \frac{\hbar}{2} \beta$, $S_x \beta = \frac{\hbar}{2} \alpha$, and defining

$\delta_{i,j} = \delta_{1,(j \pm 1)}$, one obtains

$$\langle \sigma_m / S_x / \sigma_m \rangle = \frac{\hbar}{2} \delta_{m,m'}$$

$$\langle \eta_1 / I_x / \eta_1 \rangle = \sum_{r,r'} \frac{\hbar}{2} h_r h_{r'} \delta_{r,r'}$$

$$\langle \eta_2 / I_x / \eta_2 \rangle = \sum_{s,s'} \frac{\hbar^2}{2} h_s h_{s'} \delta_{s,s'}$$

$$\langle \xi_2 / S_x / \xi_2 \rangle = \sum_{n,n'} \frac{\hbar^2}{2} g_n g_{n'} \delta_{n,n'}$$

Inserting these integrals gives

$$\begin{aligned} H_{mm'}^{\xi 1}(1x) &= \frac{\hbar}{2} \xi_{22} \delta_{m,m'} [\eta_{22} D_A^1 \frac{\hbar}{2} \sum_{r,r'} h_r h_{r'} \delta_{r,r'} + \eta_{11} D_B^1 \sum_{s,s'} h_s h_{s'} \\ &+ \frac{\hbar}{2} \delta_{s,s'}] + \delta_{m,m'} \frac{\hbar}{2} \sum_{n,n'} g_n g_{n'} \delta_{n,n'} [\eta_{22} D_A^2 \frac{\hbar}{2} \sum_{r,r'} \\ &h_r h_{r'} \delta_{r,r'} + \frac{\hbar}{2} \eta_{11} D_B^2 \sum_{s,s'} h_s h_{s'} \delta_{s,s'}] \end{aligned}$$

The $H_{mm'}^{\xi 1}(1y)$ and $H_{mm'}^{\xi 1}(1z)$ contributions may be obtained in a similar manner and combined with $H_{mm'}^{\xi 1}(1x)$ to give

$$\begin{aligned} H_{mm'}^{\xi 1}(1) &= \frac{\hbar^2}{4} \delta_{m,m'} [D_A^1 22W_1 + D_B^1 11W_2] - (-1)^{m'+1} \delta_{m,m'} \\ &[D_A^1 22W_5 + D_B^1 11W_6] + \delta_{m,m'} [U_1 (D_A^2 22W_1 + D_B^2 11W_2) \\ &+ U_2 (D_A^2 22W_3 + D_B^2 11W_4) + U_3 (D_A^2 22W_5 + D_B^2 11W_6)] \end{aligned}$$

where

$$W_1 = \sum_{r,r'} h_r h_{r'} \delta_{r,r'} ; \quad W_2 = \sum_{s,s'} h_s h_{s'} \delta_{s,s'}$$

$$W_3 = \sum_{r,r'} (-1)^{r'+1} h_r h_{r'} \delta_{r,r'} ; \quad W_4 = \sum_{s,s'} (-1)^{s'+1} h_s h_{s'} \delta_{s,s'}$$

$$W_5 = \sum_{r,r'} (-1)^{r'+1} h_r h_{r'} \delta_{r,r'} ; \quad W_6 = \sum_{s,s'} (-1)^{s'+1} h_s h_{s'} \delta_{s,s'}$$

$$U_1 = \sum_{n,n'} g_n g_{n'} \delta_{n,n'} \quad ; \quad U_2 = \sum_{n,n'} (-1)^{n'+1} g_n g_{n'} \delta_{n,n'}$$

$$U_3 = \sum_{n,n'} (-1)^{n'+1} g_n g_{n'} \delta_{n,n'} \quad ; \quad U_4 = \sum_{m,m'} g_m g_{m'} \delta_{m,m'}$$

$$U_5 = \sum_{m,m'} g_m g_{m'} (-1)^{m'+1} \delta_{m,m'} \quad ; \quad U_6 = \sum_{m,m'} g_m g_{m'} (-1)^{m'+1} \delta_{m,m'}$$

$$V_2 = \sum_{nm} g_n g_m \delta_{n,m} \quad ; \quad V_3 = \sum_{nm} g_n g_m (-1)^{m'+1} \delta_{m,n}$$

$H_{mm}^{\xi 1}(2)$ can be written as

$$\begin{aligned} H_{mm}^{\xi 1}(2) &= \langle \psi_1 \psi_2 \sigma_m \xi_2 \eta_1 \eta_2 / \vec{S}_1 \cdot (\delta_{1A} \vec{I}_A + \delta_{1B} \vec{I}_B) / \psi_2 \psi_1 \xi_2 \sigma_m \eta_1 \eta_2 \rangle \\ &\quad + \langle \psi_1 \psi_2 \sigma_m \xi_2 \eta_1 \eta_2 / \vec{S}_2 \cdot (\delta_{2A} \vec{I}_A + \delta_{2B} \vec{I}_B) / \psi_2 \psi_1 \xi_2 \sigma_m \eta_1 \eta_2 \rangle \\ &= S_{12} [\langle \sigma_m / \vec{S} / \xi_2 \rangle \langle \xi_2 / \sigma_m \rangle + \langle \sigma_m / \xi_2 \rangle \langle \xi_2 / \vec{S} / \sigma_m \rangle] \cdot \\ &\quad [D_A^{12} \eta_{22} \langle \eta_1 / \vec{I} / \eta_1 \rangle + D_B^{12} \eta_{11} \langle \eta_2 / \vec{I} / \eta_2 \rangle] \end{aligned}$$

where $D_A^{12} = \langle \psi_1 / \delta_A / \psi_2 \rangle$; $D_B^{12} = \langle \psi_1 / \delta_B / \psi_2 \rangle$.

As before one may write

$$H_{mm}^{\xi 1}(2) = H_{mm}^{\xi 1}(2x) + H_{mm}^{\xi 1}(2y) + H_{mm}^{\xi 1}(2z) \quad \text{where, for example,}$$

$$\begin{aligned} H_{mm}^{\xi 1}(2x) &= S_{12} [\langle \sigma_m / S_x / \xi_2 \rangle \langle \xi_2 / \sigma_m \rangle + \langle \sigma_m / \xi_2 \rangle \langle \xi_2 / S_x / \sigma_m \rangle] \cdot \\ &\quad [D_A^{12} \eta_{22} \langle \eta_1 / I_x / \eta_1 \rangle + D_B^{12} \eta_{11} \langle \eta_2 / I_x / \eta_2 \rangle] \end{aligned}$$

which becomes, on carrying out the integrations,

$$H_{mm}^{\xi 1}(2x) = \frac{\hbar^2}{4} S_{12} \sum_{n,n'} g_n g_{n'} [\delta_{m,m'} \delta_{nm'} + \delta_{mn'} \delta_{n,m'}]$$

$$\cdot [D_A^{12} \eta_{22} W_1 + D_B^{12} \eta_{11} W_2].$$

The $H_{mm}^{\xi 1, (2y)}$ and $H_{mm}^{\xi 1, (2z)}$ contributions may be obtained in a similar manner to give,

$$\begin{aligned} H_{mm}^{\xi 1, (2)} = & \frac{\hbar^2}{4} S_{12} [\Sigma_{n,n'} g_n g_{n'} (\delta_{m,m'} \delta_{nm'} + \delta_{mn'} \delta_{n,n'}) \cdot \\ & (D_A^{12} \eta_{22} W_1 + D_B^{12} \eta_{11} W_2) - \Sigma_{n,n'} g_n g_{n'} ((-1)^{n'+1} \delta_{m,n'} \delta_{nm'} \\ & + (-1)^{m'+1} \delta_{mn'} \delta_{n,m'}) (D_A^{12} \eta_{22} W_3 + D_B^{12} \eta_{11} W_4) + \Sigma_{n,n'} \\ & g_n g_{n'} ((-1)^{n'+1} \delta_{mn'} \delta_{nm'} + (-1)^{m'+1} \delta_{nm'} \delta_{mn'}) \\ & (D_A^{12} \eta_{22} W_5 + D_B^{12} \eta_{11} W_6)] \end{aligned}$$

Combining $H_{mm}^{\xi 1, (1)}$ and $H_{mm}^{\xi 1, (2)}$ gives finally,

$$\begin{aligned} H_{mm}^1 = & \frac{\hbar^2}{4} \left\{ \delta_{m,m'} \xi_{22} [D_A^1 \eta_{22} W_1 + D_B^1 \eta_{11} W_2] + (-1)^{m'+1} \delta_{m,m'} \xi_{22} \right. \\ & [D_A^1 \eta_{22} W_3 + D_B^1 \eta_{11} W_4] + (-1)^{m'+1} \delta_{mm'} \xi_{22} [D_A^1 \eta_{22} W_5 + D_B^1 \eta_{11} W_6] \\ & + \delta_{mm'} [U_1 (D_A^2 \eta_{22} W_1 + D_B^2 \eta_{11} W_2) + U_2 (D_A^2 \eta_{22} W_3 + D_B^2 \eta_{11} W_4) \\ & + U_3 (D_A^2 \eta_{22} W_5 + D_B^2 \eta_{11} W_6)] \left. \right\} - \frac{\hbar^2}{4} S_{12} \left\{ \Sigma_{n,n'} g_n g_{n'} \right. \\ & [\delta_{m,n'} \delta_{nm'} + \delta_{mn'} \delta_{n,m'}] \cdot [D_A^{12} \eta_{22} W_1 + D_B^{12} \eta_{11} W_2] \\ & - [(-1)^{n'+1} \delta_{m,n'} \delta_{nm'} + (-1)^{m'+1} \delta_{n,m'} \delta_{mn'}] \\ & [D_A^{12} \eta_{22} W_3 + D_B^{12} \eta_{11} W_4] + [(-1)^{n'+1} \delta_{mn'} \delta_{nm'} + (-1)^{m'+1} \\ & \left. \delta_{nm'} \delta_{mn'}] [D_A^{12} \eta_{22} W_5 + D_B^{12} \eta_{11} W_6] \right\}. \end{aligned}$$

But it can be readily shown that W_3 , W_4 and U_2 are all

zero and $H_{mm'}^{\xi 1}$ reduces to

$$\begin{aligned}
 H_{mm'}^{\xi 1} = & \frac{\hbar^2}{4} \left\{ \delta_{m,m'} \xi_{22} [D_A^1 \eta_{22} W_1 + D_B^1 \eta_{11} W_2] + (-1)^{m'+1} \delta_{m,m'} \right. \\
 & [D_A^1 \eta_{22} W_5 + D_B^1 \eta_{11} W_6] + \delta_{m,m'} (U_1 [D_A^2 \eta_{22} W_1 + D_B^2 \eta_{11} W_2] \\
 & + U_3 [D_A^2 \eta_{22} W_5 + D_B^2 \eta_{11} W_6]) - S_{12} \Sigma_{n,n'} g_n g_{n'} \\
 & ([\delta_{nm}, \delta_{m,n'} + \delta_{mn}, \delta_{n,m'}] [D_A^{12} \eta_{22} W_1 + D_B^{12} \eta_{11} W_2] \\
 & + [(-1)^{n'+1} \delta_{mn}, \delta_{nm} + (-1)^{m'+1} \delta_{nn}, \delta_{nn'}] \\
 & \left. [D_A^{12} \eta_{22} W_5 + D_B^{12} \eta_{11} W_6] \right\}.
 \end{aligned}$$

In an analogous manner the general matrix element of the other matrices maybe reduced to

$$\begin{aligned}
 H_{nn'}^{\xi 2} = & \frac{\hbar^2}{4} \left\{ \delta_{n,n'} \xi_{11} [D_A^2 \eta_{22} W_1 + D_B^2 \eta_{11} W_2] + (-1)^{n+1} \delta_{nm', 11} \right. \\
 & [D_A^2 \eta_{22} W_5 + D_B^2 \eta_{11} W_6] + \delta_{nn'} (U_4 [D_A^1 \eta_{22} W_1 + D_B^1 \eta_{11} W_2] \\
 & + U_6 [D_A^1 \eta_{22} W_5 + D_B^1 \eta_{11} W_6]) - S_{12} \Sigma_{m,m'} g_m g_{m'} \\
 & ([\delta_{nm}, \delta_{m,n'} + \delta_{n,m}, \delta_{mn}] [D_A^{12} \eta_{22} W_1 + D_B^{12} \eta_{11} W_2] \\
 & + [(-1)^{n'+1} \delta_{nm}, \delta_{mn} + (-1)^{m'+1} \delta_{nn}, \delta_{nm'}] \\
 & \left. [D_A^{12} \eta_{22} W_5 + D_B^{12} \eta_{11} W_6] \right\}
 \end{aligned}$$

$$\begin{aligned}
 H_{rr'}^{\eta 1} = & \frac{\hbar^2}{4} \left\{ \delta_{r,r'} \eta_{22} [D_A^1 \xi_{22} U_4 + D_A^2 \xi_{11} U_1 - 2D_A^{12} S_{12} V_1 V_2] \right. \\
 & + (-1)^{r'+1} \delta_{rr'} \eta_{22} [D_A^1 \xi_{22} U_6 + D_A^2 \xi_{11} U_3 - 2D_A^{12} S_{12} V_1 V_3] \\
 & + \delta_{rr'} (W_2 [D_B^1 \xi_{22} U_4 + D_B^2 \xi_{11} U_1 - 2D_A^{12} S_{12} V_1 V_2] + W_6
 \end{aligned}$$

$$\begin{aligned}
& [D_B^1 \xi_{22} U_6 + D_B^2 \xi_{11} U_3 - 2D_B^{12} S_{12} V_1 V_3]) \} \\
H_{ss'}^2 = & \frac{n^4}{4} \{ \delta_{s,s'} \eta_{11} [D_B^1 \xi_{22} U_4 + D_B^2 \xi_{11} U_1 - 2D_B^{12} S_{12} V_1 V_2] \\
& + (-1)^{s'+1} \delta_{s',11} [D_B^1 \xi_{22} U_6 + D_B^2 \xi_{11} U_3 - 2D_B^{12} S_{12} V_1 V_3] \\
& + \delta_{ss'} (W_1 [D_A^1 \xi_{22} U_4 + D_A^2 \xi_{11} U_1 - 2D_A^{12} S_{12} V_1 V_2] \\
& + W_5 [D_A^1 \xi_{22} U_6 + D_A^2 \xi_{11} U_3 - 2D_A^{12} S_{12} V_1 V_3]) \}
\end{aligned}$$

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